THE EFFECT OF SUBSTITUENTS ON THE COORDINATION OF NITROGEN-CONTAINING LIGANDS

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by

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ABSTRACT

A wide range of complexes of divalent and trivalent iron, ruthenium and osmium containing coordinated 2,2'-bipyridine have been prepared.

These are all six coordinate and are of general formulae $(M(bipy)_3)^{n+}$, $(M(bipy)_2X_2)^{n+}$, $(M(bipy)_2XY)^{n+}$ $(M(bipy)X_4)^{n\pm}$, $(M(bipy)X_2Y_2)^{n\pm}$, where X and Y include a wide range of monodentate and bidentate ligands including cyanide, oxalate, ammonia, pyridine and the halogens. Several complexes containing 4,4'-dimethylbipyridine have also been prepared.

The electronic absorption spectra of these complexes in solution have been measured, and a number of assignments made for the observed transitions. Both the divalent and the trivalent complexes show intense intraligand transitions of bipyridyl in the ultraviolet region. In the visible region, the divalent complexes show intense metal to ligand charge transfer transitions, while the trivalent complexes exhibit ligand to metal charge transfer transitions of different types.

The effects of such factors as the metal ion, the charge on the metal ion, substituents in the bipyridyl ligand and the presence of coordinated ligands other than bipyridyl have been discussed, and the results of this

work related to earlier studies.

Proton magnetic resonance spectra of some divalent complexes containing 4,4'-dimethylbipyridine have been measured, and these are correlated with the electronic absorption spectra where possible.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The electronic absorption spectra of transition metal complexes have been studied by many workers. There are three main types of bands, some or all of which may occur in the visible and ultraviolet spectral regions. They are;

a. Ligand field bands of low intensity which are Laporte forbidden transitions involving the d-orbitals of the metal.

b. Intra-ligand bands, generally of high intensity, which are also observed in the free ligand, and are transitions involving orbitals localised on the ligand.

c. Charge transfer bands, also often of high intensity, which are not present in either the free ligand or the free metal ion. These are transitions in which an electron is transferred from an orbital localised on the metal to an orbital localised on the ligand, or the reverse.

Of these three types of transitions, ligand field bands have been extensively studied, and they can generally be understood in terms of ligand field theory. However, it is only recently that there has been much interest in charge transfer and intra-ligand spectra. The range of complexes which have been studied in detail, either theoretically or experimentally, is small, and there have been few

systematic studies of such factors as the effects of metal ion, metal ion charge, substituents in the ligands, and the presence of other ligands not directly involved in the charge transfer transitions in the coordination sphere.

Molecular orbital theory is necessary for a theoretical understanding of charge transfer and intra-ligand spectra, but the complexity of the systems involved gives rise to many difficulties in calculations (some of which are discussed in Chapter II).

There is an alternative approach which can give at least a qualitative understanding of the transitions. This involves taking a closely related series of complexes and studying the effects of changes in such factors as coordinated ligands, substituents and metal ion on the spectra. This can then be related to earlier work and to other non-spectroscopic data, and should enable assignments to be made for some of the bands, and give some idea of the factors that influence the spectra. This was the approach adopted in the present work.

Heterocyclic ligands such as pyridine, 2,2'-bipyridine (see Fig.1) and 1,10-phenanthroline have been found to form stable complexes with many transition metals. Many of these complexes show both intra-ligand and charge transfer transitions in the visible and ultraviolet spectral regions.

The divalent and trivalent complexes of iron, ruthenium and osmium with 2,2'-bipyridine are very suitable in this respect. It is also possible to prepare quite a large range of complexes of these metals of general formulae $(M(bipy)_3)^{n+}$, $(M(bipy)_2XY)^{n+}$, $(M(bipy)X_2Y_2)^{n+}$ where X and Y include a wide range of bidentate and monodentate ligands (see Table 1).

The present work describes the preparation of a number of such complexes, both ones previously reported in the literature and new ones. These preparative studies are described in Chapter I.

The ultraviolet and visible absorption spectra of these complexes were then studied, and are described in Chapters III and IV. Both the divalent and the trivalent metal complexes showed the intraligand transitions of bipyridyl in the ultraviolet region. In the visible, the trivalent complexes showed metal-reduction charge transfer spectra, while the divalent complexes showed metal oxidation bands. The observed energy changes in the spectra could, in some cases, be related to such factors as the metal ion present, or the ligand field strength of the coordinated ligands.

The results obtained in this work are briefly discussed

with reference to previous work on systems involving other metal ions in Chapter V. Chapter VI discusses the proton magnetic resonance spectra of complexes containing 4,4'-dimethyl-bipyridine.

CHAPTER I

PREPARATIVE STUDIES

INTRODUCTION

In recent years there has been considerable interest shown in the preparation and properties of complexes of iron, ruthenium and osmium, with ligands such as 2,2'-bipyridyl* and 1,10-phenanthroline. A number of preparative routes to these complexes have been reported, and are discussed in Part 1 of this chapter.

The preparative studies carried out in the present work are described in Parts 2, 3 and 4. In Part 2 the preparation of new compounds of divalent and trivalent iron, ruthenium and osmium with bipyridyl are discussed. Part 3 contains a discussion of the complexes of iron, ruthenium and osmium prepared with the substituted bipyridyls, 4,4'-dimethylbipyridine and 4,4'-diphenylbipyridine. The experimental details of the preparative work are given in Part 4. Finally, the reactions and compounds produced in the preparation of potassium pentachloroaquoruthenate (III), $K_2RuCl_5H_2O$, are discussed in Part 5. This compound is an important starting material for the preparation of ruthenium complexes.

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* Hence abbreviated to "bipyridyl"

1. Review of Previous Work

Iron (II). Bis-bipyridyl complexes

The intensely red coloured complex cation $(Fe(bipy)_3)^{2+}$ has been known since 1898.[1] Mono- and bis-complexes of 2,2'-bipyridyl were postulated as intermediates in the formation of the tris-complexes.[2] Recent workers have isolated an extensive series of complexes which may be formulated as $(Fe(amine)_2X_2)^{n+}$, where the amine is 2,2'-bipyridyl or 1,10-phenanthroline, and X_2 includes a wide range of monodentate and bidentate ligands. These complexes have recently been reviewed by E. Konig.[3]

When the ligand X produces a strong ligand field (e.g. $X = CN^-$) the complexes are spin paired and diamagnetic, but with weak field ligands (e.g. $X = Cl^-$) they are spin free. Some complexes show intermediate magnetic behaviour at room temperature, (e.g. $(Fe(bipy)_2C_2O_4)$ has $\mu = 3.76$ B.M. [4]) while the thiocyanate complex $(Fe(bipy)_2(SCN)_2)$, is spin-free at high temperatures and spin-paired at low temperatures. In solution the spin free complexes (e.g. $(Fe(bipy)_2Cl_2)$) rapidly disproportionate to the diamagnetic tris-complex. The greater stability of the tris-complex is attributed to orbital stabilisation resulting from spin pairing.[2,3]

Iron (II). Mono-bipyridyl complexes

Few mono-bipyridyl complexes of iron (II) are known. The complex $K_2\{Fe(bipy)(CN)_4\}$ [5] has been well characterised and is stable in aqueous and acid solution. It is spin paired and shows no tendency to disproportionate.

Broomhead and Dwyer [6] have prepared a complex formulated as $(Fe(bipy)Cl_2)$ by reacting bipyridyl with a large excess of ferrous chloride in one normal hydrochloric acid. Vacuum pyrolysis of tris-bipyridyl iron (II) halides has produced compounds formulated as $(Fe(bipy)Cl_2)$ and $(Fe(bipy)Br_2)$ [7]. However the preparations are often not reproducible, complexes of varying stoichiometry being obtained. It has been shown that pyrolysis techniques may lead to a mixture of products. [8,9] The compounds are spin free and readily revert to the tris-bipyridyl cation in solution. They would be unlikely to be simple octahedral complexes, and until further data are available their stoichiometry and formulation remain uncertain.

Iron (III)

The trivalent complex ions $(Fe(bipy)_3)^{3+}$, $(Fe(bipy)_2(CN)_2)^{+}$, and $(Fe(bipy)(CN)_4)^{-}$ can all be prepared by oxidation of the corresponding divalent compound. The compounds all contain spin paired iron and are readily reduced, especially in solution.

There have been several attempts to prepare the ferric complexes directly from iron (III). Harris and Lockyer [10] prepared spin free complex cation, $(Fe^{III}(phen)_2Cl_2)^+$ by reacting 1,10 phenanthroline with anhydrous ferric chloride in glacial acetic acid. Attempts to prepare the trivalent complexes in aqueous solution have led to the formation of binuclear species which appear to have either a hydroxy- or an oxy-bridge linkage[11,12,13]. Driver and Walker[11], and Anderegg[12] postulate the formula $(Fe_2(OH)_2L_4)^{4+}$, L = bipy, phen. However, Khedekar et al[13] formulate the compounds as $(Fe_2OL_4)X_2Y_2.nH_2O$, i.e. with an oxo-linkage. In the absence of more conclusive evidence definite assignment of a structure is not yet possible.

Broomhead and Dwyer[6] have reported the preparation of a yellow trivalent mono-bipyridyl complex from the reaction of ferric chloride and bipyridyl in dimethylformamide, but they give no analytical data or physical measurements.

Harris and Lockyer[10] have reported the preparation of $(N(C_2H_5)_4)(Fe\ phen\ Cl_4)$ from the reaction of 1,10-phenanthroline with $N(C_2H_5)_4(FeCl_4)$ in an acetone-dioxan mixture. This compound is spin free, and undergoes auto-reduction followed by disproportionation to give the ion $(Fe(bipy)_3)^{2+}$ in solution.

Ruthenium (II). Bis-bipyridyl complexes

As is the case for iron, the divalent tris complex cation, $(Ru(bipy)_3)^{2+}$, has been known for some time,[14,15,16] but the isolation of bis-bipyridyl and bis-1,10-phenantholine complexes of ruthenium is a more recent development. The complex $(Ru(bipy)_2Cl_2)$ can be prepared in low yield by pyrolysis in vacuo of $(Ru(bipy)_3)Cl_2.6H_2O$.[17] Dwyer et al [18] prepared $(bipy\ H)(Ru(bipy)Cl_4)$ by the addition of bipyridyl to $K_2RuCl_5H_2O$ in acid. Pyrolysis of the former compound gives $(Ru(bipy)_2Cl_2)$.[19] It can also be formed in high yield by heating $(bipy\ H)(Ru(bipy)Cl_4)$ under reflux in dimethylformamide.[20]

Since all the ruthenium complexes are spin paired, they show little tendency to undergo the disproportionation reactions of the spin-free iron complexes. For this reason $(Ru(bipy)_2Cl_2)$ and $(Ru(phen)_2Cl_2)$ are suitable as precursors for the preparation of further ruthenium (II) complexes. The halide ions are readily replaced in aqueous solution,[21] while the bipyridyl ligands show little tendency to undergo replacement reactions. Quite an extensive series of compounds of the type $(Ru^{II}(amine)_2XY)^{n+}$ have now been prepared.[19,20,21,22] by reacting the appropriate ligand with $(Ru(bipy)_2Cl_2)$ or $(Ru(phen)_2Cl_2)$ in an aqueous medium.

Mono Bipyridyl complexes

Oxidation of $(bipy\ H)(Ru(bipy)Cl_4)$ with chlorine gives a black, insoluble compound $(Ru(bipy)Cl_4)$.[18] In the presence of alcohol which acts as a reducing agent for $(Ru(bipy)Cl_4)$, the halides can progressively be replaced by other ligands such as pyridine to give mono-bipyridyl complexes with ruthenium in both the divalent (e.g. $(Ru(bipy)(py)_4)^{2+}$) and the trivalent states [18] (e.g. $(Ru(bipy)(acac)_2)^{+}$).

Ruthenium (III)

The blue tris-bipyridyl ruthenium (III) cation can be obtained in solution by oxidation of the corresponding ruthenium (II) derivative with a strong oxidising agent (E_0 > 1.2eV). The oxidation potential and reaction kinetics for this reaction have been studied. [23,24,25,26] However, the complex has not been isolated in the solid state.

A number of trivalent mono-bipyridyl complexes are known. They include $K(Ru(bipy)Cl_4)$, $K(Ru(bipy)Br_4)$, $(Ru(bipy)(acac)_2)Cl$ $(Ru(bipy)acac\ Cl_2)$, and $(Ru(bipy)py_2X_2)^{+}$ X = Cl, Br, I. [18] Of these, the tetrahalides and the acetylacetone derivatives are quite stable in aqueous and alcoholic solutions.

However, very few bis bipyridyl ruthenium (III) derivatives are known. The complex $(Ru(bipy)_2Cl_2)Cl$ has been prepared by oxidation of $(Ru(bipy)_2Cl_2)$ with chlorine.[17] Brandt et al [27] isolated the green complex, $(Ru(bipy)_2(H_2O)_2).(ClO_4)_3$.

Osmium

Buckingham et al [28,29,30] have made extensive studies of the preparation of bipyridyl and 1,10-phenanthroline complexes of osmium. Very little other significant work has been done.

Osmium. Mono-Bipyridyl complexes

The mono-bipyridyl complexes are very similar to the ruthenium derivatives. The complexes $K(Os(bipy)Cl_4)$, and in some cases $(Os(bipy)Cl_4)$, are used as precursors for the preparation of a range of compounds very similar to those known for ruthenium.

Osmium. Bis-Bipyridyl complexes

The complex $(Os(bipy)_2Cl_2)$ is prepared by a route different from that used for the ruthenium analog. The preparation can be represented by the reaction scheme

$$K_2Os\ Cl_6 + 2\ Bipy \xrightarrow[\text{Heat}]{\text{D.M.F.}} (Os(bipy)_2Cl_2)Cl$$

$$\downarrow \quad \text{sodium dithionite}$$

$$(Os(bipy)_2Cl_2)$$

From this, further bis-bipyridyl osmium complexes can be prepared by a method similar to that used for the ruthenium complexes. However, because the halide ions in the osmium complex seem less labile, longer reaction times or more extreme conditions are required.

Osmium (III)

The range of complexes of osmium (III) known is much greater than the range known for ruthenium (III). The bis halide compounds, $(Os(bipy)_2X_2)X$ $(X = Cl^-, Br^-, I^-)$,[7] are all stable in aqueous solution. $(Os(bipy)_3)^{3+}$ can be isolated in the solid state, though it undergoes auto-reduction in solution. Trivalent complexes of osmium containing ligands such as bipyridyl, 1,10-phenanthroline, and pyridine in various combinations can also be isolated. Other complexes known include $(Os(bipy)_2pyX)^{2+}$, $(Os\ bipy(py)_3X)^{2+}$, $(X = Cl, Br, I)$ and $(Os(bipy)_2acac)^{2+}$.[28,29]

TABLE I

Complexes prepared in the course of this study.

	Iron (II)	Iron (III)
Tris	$(Fe(bipy)_3)Cl_2.6H_2O$	$(Fe(bipy)_3)(ClO_4)_3$
Bis	$(Fe(bipy)_2(CN)_2)3H_2O$	$(Fe(bipy)_2(CN)_2)NO_3.4H_2O$
		$(Fe(bipy)_2Cl_2)(Fe\ Cl_4)$*
Mono	$K_2(Fe(bipy)(CN)_4)3H_2O$	$H(Fe(bipy)(CN)_4).2H_2O$

	Ruthenium (II)	Ruthenium (III)
Tris	$(Ru(bipy)_3)Cl_2.6H_2O$	$(Ru(bipy)_3)^{3+}$ †
Bis	$(Ru(bipy)_2Cl_2)H_2O$*	$(Ru(bipy)_2Cl_2)Cl.2H_2O$
	$(Ru(bipy)_2(CN)_2)2H_2O$*	
	$(Ru(bipy)_2C_2O_4)4H_2O$	
	$(Ru(bipy)_2(NO_2)_2)2H_2O$*	
	$(Ru(bipy)_2(SCN)_2)$*	
	$(Ru(bipy)_2en)(ClO_4)_2$*	
	$(Ru(bipy)_2(NH_3)_2)(ClO_4)_2.3H_2O$*	
	$(Ru(bipy)_2(py)_2)(ClO_4)_2$	$(Ru(bipy)_2(py)_2)^{3+}$ †
	$(Ru(bipy)_2pyCl)ClO_4.3H_2O$	
	$(Ru(bipy)_2acac)Cl.3H_2O$	$(Ru(bipy)_2acac)(ClO_4)_2.H_2O$*
		$(Ru(bipy)_2(H_2O)_2)(ClO_4)_3$*

Mono	$(Ru(bipy)(py)_4)(ClO_4)_2$	$(Ru(bipy)(py)_4)^{3+}$ †
	$(Ru(bipy)(py)_2Cl_2).H_2O$	$(Ru(bipy)(py)_2Cl_2)ClO_4.3H_2O$
	$(Ru(bipy)(py)_2Br_2).2H_2O$	
	$(Ru(bipy)(py)_2I_2).2H_2O$	
	$(Ru(bipy)(acac)_2)$	$(Ru(bipy)(acac)_2)Cl.3H_2O$
		$(Ru(bipy)acacCl_2).H_2O$
	$(Ru(bipy)Cl_4)^{2-}$ †	$K(Ru(bipy)Cl_4).H_2O$
	$(Ru(bipy)Br_4)^{2-}$ †	$K(Ru(bipy)Br_4).H_2O$

	Osmium (II)	Osmium (III)
Tris	$(Os(bipy)_3)(ClO_4)_2.2H_2O$	$(Os(bipy)_3)(ClO_4)_3$
Bis	$(Os(bipy)_2Cl_2)H_2O$	$(Os(bipy)_2Cl_2)Cl.2H_2O$
	$(Os(bipy)_2(py)_2)(ClO_4)_2$	$(Os(bipy)_2(py)_2)(ClO_4)_3$
	$(Os(bipy)_2phen)(ClO_4)_2H_2O$	$(Os(bipy)_2phen)(ClO_4)_3.2H_2O$
	$(Os(bipy)_2acac)Cl.3H_2O$	$(Os(bipy)_2acac)(ClO_4)_2.H_2O$*
	$(Os(bipy)_2en)(ClO_4)_2$	
	$(Os(bipy)_2C_2O_4).3H_2O$	
	$(Os(bipy)_2pyCl)I.H_2O$	
	$(Os(bipy)_2pyBr)I.H_2O$	
	$(Os(bipy)_2(SCN)_2).2H_2O$*	
	$(Os(bipy)_2(CN)_2).3H_2O$*	
Mono		$K(Os(bipy)Cl_4).4H_2O$
	$(Os(bipy)(py)_4)(ClO_4)_2.2H_2O$	
	$(Os(bipy)(en)_2)(ClO_4)_2$	
		$(Os(bipy)(acac)_2)ClO_4.3H_2O$

4,4'-dimethylbipyridyl complexes

Iron

$(Fe(4,4'\text{-diMebipy})_3)Cl_2 . 6H_2O$

$(Fe(4,4'\text{-diMebipy})_2(CN)_2) . CHCl_3$*

$K_2(Fe(4,4'\text{-diMebipy})(CN)_4) . 4H_2O$*

Ruthenium

$(Ru(4,4'\text{-diMebipy})_3)(ClO_4)_2 . 2H_2O$

$(Ru(4,4'\text{-diMebipy})_2Cl_2) . H_2O$*

$(Ru(4,4'\text{-diMebipy})_2(CN)_2) . 4H_2O$*

$(Ru(4,4'\text{-diMebipy})_2NH_3)_2)(ClO_4)_2 . 2H_2O$*

$(Ru(4,4'\text{-diMebipy})_2acac)Cl . 2H_2O$*

$(Ru(4,4'\text{-diMebipy})_2(NO_2)_2) . H_2O$*

Osmium

$(Os(4,4'\text{-diMebipy})_3)(ClO_4)_2 . 2H_2O$*

$(Os(4,4'\text{-diMebipy})_3)(ClO_4)_3 . 3H_2O$*

* New compounds or prepared by a new method.

† Prepared in solution only.

2. Preparation of New Complexes

In this section the preparative studies on the complexes of bipyridyl with iron, ruthenium and osmium made in the course of this work are discussed. A list of the complexes prepared is given in Table I. Only those complexes which are new or which have been prepared by methods different from those outlined in the literature will be discussed in any detail. In several cases, although numerous attempts were made, certain desired complexes could not be isolated. A discussion of a number of these systems is also included in this section.

Iron (II). Bis-bipyridyl complexes

Many bis-bipyridyl iron (II) complexes have been reported. [3] However the spin free complexes disproportionate readily in solution, and their spectra must be measured in the solid state. Unfortunately, in spite of repeated efforts, it was not possible to obtain good solid state, e.g. diffuse reflectance, spectra of the intense charge transfer bands. For this reason little attempt was made to prepare these complexes.

Early in this work a number of attempts were made to prepare the bis-thiocyanate complex of iron (II), $(Fe(bipy)_2(SCN)_2)$, by methods reported at that time.[31,32,33,34]

These involved:

(i) preparation of the complex from $(Fe(py)_4(SCN)_2)$ (which has since been found to consist of a mixture of compounds [35,36]) in pyridine or chloroform.

(ii) heating the tris-complex $(Fe(bipy)_3)(SCN)_2$ in vacuo.

(iii) preparation in aqueous media.

Several compounds with varying analyses and infra-red spectra were obtained.

Calculated for $(Fe(bipy)_2(SCN)_2)$ C = 54.5, H = 3.3%.

C%	H%	Method	ν(C-N)(cm^{-1})
50.48	3.75	(i)	2106
57.51	3.84	(ii)	2060
49.30	4.16	(iii)	2060 (br)

Conductivity measurements indicated decomposition in solution. In nitrobenzene, the conductivity is high and there is a gradual increase with time, although the compound is expected to be a nonelectrolyte.

Time	Λ $ohms^{-1}$ $mole^{-1}$ cm^2 (assuming $(Fe(bipy)_2(SCN)_2)$)
0	17.3
5 mins.	20.5
2 days	26.3.

Ultraviolet and visible spectra were also not consistent

from preparation to preparation. It was concluded that the complex is unstable in solution and that in many preparations mixtures of compounds were being produced. Later studies have shown this is often the case, and the complex has recently been well characterised. [37,38,39,40,3]

Iron (II).

The complex, $(Fe(bipy)_2Cl_2)(FeCl_4)$ was prepared in a similar manner to that used for the analogous 1,10-phenanthroline complex by Harris and Lockyer.[10] The yellow complex was found to be quite stable in dry, non-aqueous solvents, but in water reduction followed by disproportion occurred to give the red $(Fe(bipy)_3)^{2+}$ cation. The complex was found to be a 1:1 electrolyte in dimethylformamide (Λ_{25^0C} = 63.3 $ohms^{-1}moles^{-1}cm^2$), but the conductivity was considerably higher in methanol indicating perhaps some dissociation of the $(FeCl_4)^-$ ion.

Ruthenium (II). Bis-bipyridyl complexes

As mentioned in Part 1, the complex $(Ru(bipy)_2Cl_2)$ is an important starting material in the preparation of other ruthenium (II) compounds. A new method for the preparation of this compound was developed.

A suspension of $(bipyH)(RubipyCl_4)$ in dilute

hydrochloric acid was reduced with zinc. The divalent bis-bipyridyl complex so formed was purified by recrystallisation from aqueous solution in the presence of excess lithium chloride. This method is also applicable to the preparation of dimethyl-substituted-bipyridyl complexes where other methods appear to give rise to complexes containing coordinated carbonyl (see Part 3).

A wide range of bis-bipyridyl complexes of ruthenium (II) was prepared by heating $(Ru(bipy)_2Cl_2)$ in aqueous methanol with an excess of the appropriate ligand. With ligands such as cyanide or nitrite, where the final complex is a non-electrolyte, the complexes could generally be isolated readily by evaporation of the methanol, followed by cooling. Cationic complexes were isolated as the perchlorate salts, most of these being fairly insoluble. Iodide was originally used as a precipitating anion but it was found that ligands such as ammonia, pyridine and ethylenediamine in these complexes tend to be replaced by halide ions in aqueous solution, especially when heated.

Ruthenium (III). Bis-bipyridyl complexes

Except for the chloro-complex, $(Ru(bipy)_2Cl_2)Cl$, bis-bipyridyl complexes of ruthenium (III) are unstable and difficult to isolate. Oxidation reactions of

ruthenium (II) complexes to give ruthenium (III) compounds are quite complex in many cases.

The compound $(Ru(bipy)_2(H_2O)_2)(ClO_4)_3$ was prepared by converting an aqueous methanol solution of $(Ru(bipy)_2Cl_2)$ to the diaquo-complex, $(Ru(bipy)_2(H_2O)_2)^{2+}$, by heating with excess silver nitrate. After removal of the silver chloride precipitated, the solution was heated until it turned dark blue, silver being precipitated in the reaction. The trivalent dark blue complex was isolated as the triperchlorate, $(Ru(bipy)_2(H_2O)_2)(ClO_4)_3$. However, on recrystallisation from water, it tended to go dark green, and form a compound which is less soluble in water.

The complex cation $(Ru(bipy)_2acac)^{2+}$ was formed from the complex $(Ru(bipy)_2acac)Cl$ in water by oxidation with ammonium ceric nitrate. The blue-green complex was isolated as the diperchlorate, $(Ru(bipy)_2acac)(ClO_4)_2$. However, it could not be recrystallised as it was readily reduced in solution.

The preparation does not always proceed smoothly. An excess of ceric ions is always required to effect the oxidation, but too large an excess leads to the formation of an orange-brown solution, presumably containing ruthenium (IV), which on standing gradually turns green.

Attempts at preparation of other complexes by similar

methods were unsuccessful. Oxidation of the oxalato-complex $(Ru(bipy)_2C_2O_4)$ in methand with cerium (IV) gives an orange species, perhaps ruthenium (IV), which on standing turns green. However, it was not possible to isolate a pure sample of the green compound.

The chloro-complex $(Ru(bipy)_2Cl_2)Cl$ is readily prepared, but the corresponding bromo-cation $(Ru(bipy)_2Br_2)^+$ could not be isolated. Oxidation of the divalent complex, $(Ru(bipy)_2Br_2)$ with bromine in a number of reaction media including water, dilute and concentrated hydrobromic acid failed to give a product. Oxidation with cerium (IV) and mercuric salts also failed to give a product, although an isobiestic point at 22,480 cm^{-1} could be observed when ceric ions were added to a methanol solution of $(Ru(bipy)_2Br_2)$.

Several other trivalent complexes could be prepared in solution, and their formation followed by means of visible absorption spectra. In each case the divalent complex was dissolved in either water or in a few cases methanol, and ceric ions added gradually. Visible spectra were recorded after each addition (see Figs 16 and 17). In several cases isobiestic points could be observed at energies below ~23,800 cm^{-1}, indicating the presence of only two absorbing species (cerium (IV) begins to absorb at about 23,800 cm^{-1}).

These included:

	Isobiestic point (cm^{-1})
$(Ru(bipy)_3)^{3+}$	17,540
$(Ru(bipy)_2(py)_2)^{3+}$	17,450
$(Ru(bipy)(py)_4)^{3+}$	17,790
$(Ru(bipy)_2acac)^{2+}$	16,210

Except for $(Ru(bipy)_2acac)^{2+}$, these cations were too readily reduced to be isolated.

The divalent compounds $(Ru(bipy)_2C_2O_4)$, $(Ru(bipy)_2(COOH)_2)$, $(Ru(bipy)_2(CN)_2)$, $(Ru(bipy)_2(SCN)_2)$, $(Ru(bipy)_2I_2)$ all gave orange solutions when oxidised. No isobiestic points were observed in the visible and no pure compounds could be isolated from these solutions.

Ruthenium. Mono-bipyridyl complexes

Whereas bis-bipyridyl ruthenium (II) complexes can be formed readily with a variety of ligands (see Table I), the mono-bipyridyl complexes known are restricted to pyridine, acetylacetone and halide ions as ligands. Ligands like cyanide, nitrite, thiocyanate, oxalate, and ethylenediamine were used in attempts to prepare mono-bipyridyl complexes but without success. When these ligands were reacted with aqueous ethanolic solutions of

$(Ru(bipy)Cl_4)$, pure samples of the divalent bis-bipyridyl ruthenium complexes were isolated. Attempts to isolate complexes after a shorter reaction time were also unsuccessful, a mixture of unidentified products being obtained. The reaction of bipyridyl with $K_3(Ru(C_2O_4)_3)$ and $(Ru(en)_3)^{2+}$ also failed to give mono-bipyridyl complexes.

Preparation of a nitrite complex by heating aqueous $(RubipyCl_4)$ with silver nitrite led to the formation of a product with a strong infra-red band at 1880 cm^{-1}, presumably containing coordinate nitrosyl.

An attempt was also made to prepare the divalent mono-bipyridyl tetra halogeno- complex anions, $(Ru(bipy)Cl_4)^{2-}$, $(Ru(bipy)Br_4)^{2-}$. Attempts to isolate the complexes after reduction of the corresponding trivalent complexes with hydrazine were unsuccessful, but the formation of a violet complex could be followed spectrophotometrically (see Fig.12).

Osmium. Bis-bipyridyl complexes

The osmium (II) bis-bipyridyl complexes were prepared by heating a solution of the chloro-complex, $(Os(bipy)_2Cl_2)$, with an excess of the appropriate ligand, using methods

described by Buckingham.[29] The new complexes $(Os(bipy)_2(SCN)_2)$ and $(Os(bipy)_2(CN)_2)$ were also prepared by similar methods.

Osmium. Mono-bipyridyl complexes

These were prepared by methods very similar to those described by Buckingham.[28] The starting material for the mono-bipyridyl complexes, $(Os\ bipy\ Cl_4)$ was isolated in a slightly different manner. Buckingham's method involves pyrolysis of the complex $(bipy\ H_2)(Os\ Cl_6)$. The brown residue from the pyrolysis is reduced to the soluble trivalent anion $(Os\ bipy\ Cl_4)^-$ by heating it under reflux for about twelve hours with hypophosphorous acid. A pure sample of $(Os(bipy)Cl_4)$ can then be obtained by oxidising the solution with chlorine. However, it was found that the reduction of the residue could also be effected with a solution of sodium dithionite.

It was also found that the complexes which were prepared from $K(Os\ bipy\ Cl_4)$ by Buckingham could be prepared by refluxing the appropriate ligand in an ethanolic suspension of $(Os(bipy)Cl_4)^-$ a method analogous to that used for ruthenium compounds.

3. Substituted Bipyridyl Complexes

A considerable number of complexes of iron with substituted bipyridyls has been prepared. Complexes containing methyl-substituted ligands have been studied in the greatest detail. The effects of steric interactions of substituents on the formation of complexes have been investigated.[41] Stability constants and electronic absorption spectra of many of the complexes have been measured.[41,42,43,44]

Little work has been done on ruthenium and osmium complexes, and often preparative details have not been published.[45,46]

4,4'-dimethylbipyridyl complexes

The 4,4'-dimethylbipyridyl complexes of iron are similar to the analogous bipyridyl complexes, as might be expected. The methyl groups in the 4,4'- positions (see Fig.1) will not be subject to the steric interactions found in 3,3'- and 6,6'- disubstituted bipyridyls. The electronic effects of the methyl groups are reasonably small. (pK_a pyridine = 5.17, pK_a para-methylpyridine = 6.02).[47]

Complexes of 4,4'- dimethylbipyridine with iron (II)

could be prepared by the same methods as those used for bipyridyl (see Part 4). The complex, $(Os(4,4'\text{-diMebipy})_3)(ClO_4)_2$ was also prepared by the same method as that used for the bipyridyl complex (see Part 4).

However, this is not always the case for ruthenium. The tris-complex, $(Ru(4,4'\text{-diMebipy})_3)Cl_2$ could not be prepared by heating the ligand with ruthenium trichloride to 150°c in a sealed tube. A yellow compound which was not identified was obtained. However, the less severe method of preparation from the hydroxy ruthenate $K_2(RuCl_5OH)$[15] worked well (see Part 4).

The compound $(4,4'\text{-diMebipyH})(Ru(4,4'\text{-diMebipy})Cl_4)$ can be prepared in the same way as for the unsubstituted bipyridyl complex. However, when this complex is heated under reflux in dimethyl-formamide in order to obtain the bis-complex, $(Ru(4,4'\text{-diMebipy})_2Cl_2)$, a complex which has a strong absorption at ~1950 cm^{-1}, indicating coordinated carbonyl (see Part 5), is obtained. A similar result has been observed with methyl-substituted 1,10-phenanthroline complexes.[48] Presumably the reaction involves the abstraction of a carbonyl group from the dimethyl-formamide.

However, the bis-complex, $(Ru(4,4'\text{-diMebipy})_2Cl_2)$ was

obtained by the reduction of (4,4'-diMebipy)$_2$ ($Ru(4,4'\text{-diMebipy})Cl_4$) with zinc in hydrochloric acid. Further bis-complexes could be prepared from the dichloro-complex using the methods developed for bipyridyl (see Part 4).

4,4'-diphenylbipyridyl complexes

The coordination ability of this ligand is considerably different from bipyridyl and no pure complexes of definite composition could be isolated in the course of this work. The phenyl substituents would be expected to exert much greater steric and electronic effects than the corresponding methyl groups. The ligand itself is much less soluble in alcohol or acid than bipyridyl, and in most cases this necessitated slightly different reaction conditions.

Preparation of the tris-iron complexes was attempted by adding a slight excess of the ligand in benzene to an alcoholic solution of ferrous chloride. A purple complex precipitated on the addition of ether. This was washed well with benzene to remove any excess ligand, then recrystallised several times from solvents such as dichloromethane and ethanol. However, analytical figures were not consistent, but were low in carbon, suggesting

a bis(4,4'-diphenylbipyridyl)iron complex, rather than a tris.

		C%	H%	Cl%
Calculated for				
$(Fe(4,4'\text{-diphenylbipy})_3)Cl_2$		75.2	4.56	6.75
$(Fe(4,4'\text{-diphenylbipy})_2Cl_2)$		73.7	4.31	9.69
Found	(i)	68.91	4.78	11.03
	(ii)	64.36	4.54	
	(iii)	60.04	4.36	
Calculated for				
$(Fe(4,4'\text{-diphenylbipy})_2Br_2)$		65.9	3.85	
Found		62.04	4.64	

A ligand to metal ratio of 1.8:1 was obtained from a Job titration, also suggesting a bis(4,4'-diphenylbipyridyl) complex.

The solid product which is diamagnetic is conducting in a variety of solvents. Assuming the formulation $(Fe(4,4'\text{-diphenylbipy})_2Cl_2)$ the conductivity indicated a 1:1 electrolyte.

Solvent	Conductivity ($ohms^{-1}$ $moles^{-1}$ cm^2)
Methanol	95.3
Nitrobenzene	27.2
Acetone	94.0
Acetonitrile	137

As it was not possible to isolate a compound of constant stoichiometry this work was discontinued.

A complex of ruthenium with 4,4'-diphenylbipyridyl could not be prepared by any of the methods used for $(Ru(bipy)_3)^{2+}$ or $(Ru(bipy)_2Cl_2)$. However, when this ligand was added to an alcoholic solution of ruthenium trichloride a purple-black precipitate was formed. This was recrystallised from chloroform. It is a non-electrolyte in netrobenzene, and is not decomposed by dilute acids. However, the analytical figures again failed to suggest a reasonable formulation.

	C%	H%
Calculated for		
$(Ru(4,4'\text{-diphenylbipy})Cl_2)$	54.9	4.57
$(Ru(4,4'\text{-diphenylbipy})_2Cl_2)$	67.0	5.58
$(Ru(4,4'\text{-diphenylbipy})_{1.5}Cl_2)$	62.3	5.20
$(Ru(4,4'\text{-diphenylbipy})_{1.5}Cl_3)$	59.0	4.92
Found	60.95	4.93

4. Experimental Details of Preparative Work

In this section the preparative methods used are described. Analytical figures (percentage by weight) and some other relevant data are also presented. The complexes were all dried either under vacuum or over calcium chloride, and the presence of the appropriate ligands verified by infra-red spectra.

Iron

The cyano-complexes of iron were prepared by the methods used by Schilt.[5] The reaction schemes involved in the preparations are outlined below.

$$(Fe(bipy)_3)^{2+} + KCN(\text{excess}) \xrightarrow[\text{stand 2hrs}]{H_2O} (Fe(bipy)_2(CN)_2)\downarrow$$

$$(Fe(bipy)_2(CN)_2) + KCN(\text{excess}) \xrightarrow[\text{heat gently } \sim 12\text{hrs}]{H_2O} K_2(Fe(bipy)(CN)_4)$$

$$(Fe(bipy)_2(CN)_2) + HNO_3(\text{conc}) \xrightarrow{H_2O} (Fe(bipy)_2(CN)_2)^+$$

$$K_2(Fe(bipy)(CN)_4) + Cl_2(\text{gas}) \xrightarrow{H^+} (Fe(bipy)(CN)_4)^-$$

The analytical data are given below.

Compound	Found		Calculated Analyses	
	C%	H%	C%	H%
$(Fe(bipy)_2(CN)_2)3H_2O$	56.40	4.55	55.8	4.64
$K_2(Fe(bipy)(CN)_4)3H_2O$	38.40	2.99	38.5	3.12
$(Fe(bipy)_2(CN)_2)NO_3.4H_2O$	46.96	3.99	47.4	4.33
$H(Fe(bipy)(CN)_4).2H_2O$	47.49	3.88	47.6	3.12

Dichlorobis(bipyridyl)iron(III) tetrachloroiron(III), $(Fe(bipy)_2Cl_2)(FeCl_4)$

Bipyridyl (0.156 gms) was added to anhydrous ferric chloride (.16 gms) in glacial acetic acid (10 mls). The yellow precipitate obtained was washed with glacial acetic acid.

Analysis: Found: C= 37.68, H = 2.51, N = 8.78, Cl = 33.4

Calc.for $(Fe(bipy)_2Cl_2)(FeCl_4)$

C = 38.07, H = 2.50, N = 8.30, Cl = 31.9%

Conductivity in dimethylformamide indicated a 1:1 electrolyte

$$\Lambda_{25^oc} = 63.3 \text{ ohms}^{-1} \text{ moles}^{-1} \text{ cm}^2$$

Ruthenium (II)

The complex $(bipyH)(Ru(bipy)Cl_4)$ was prepared from $K_2RuCl_5H_2O$ by the same method as that used by Bosnich and Dwyer[20] for the analogous 1,10-phenanthroline complex.

This was then converted to the bis complex $(Ru(bipy)_2Cl_2)$ by refluxing in dimethylformamide[20] or by the method described on page 29.

Further bis-complexes were prepared by heating the dichloride, $(Ru(bipy)_2Cl_2)$ with an excess of the appropriate ligand. Many of the preparations are very similar to those given for the analogous 1,10-phenanthroline complexes by Dwyer, Goodwin and Gyarfas,[19] and by Bosnich and Dwyer.[20]

Further experimental details are given in the following section. In cases where previously described techniques which involve heating of the appropriate ligand with $(Ru(bipy)_2Cl_2)$ are used only brief details are given.

In those complexes where a hydrate was indicated by the analysis, the presence of water was confirmed by infra-red spectra.

Bis-bipyridyl complexes

Dichlorobis(bipyridyl)ruthenium(II)hydrate $(Ru(bipy)_2Cl_2)H_2O$

$(bipyH)(RubipyCl_4)$ was suspended in 3 molar hydrochloric acid (25 mls). Granulated zinc (1 gm) was added, and the solution heated gently on a water bath. The solution gradually turned violet. If reaction ceased while

$(bipyH)(RubipyCl_4)$ was still present a little more hydrochloric acid was added. The solution was filtered. An excess of lithium chloride (2 gms) was added, and the solution evaporated to a small volume on a water bath. Purple $(Ru(bipy)_2Cl_2)H_2O$ crystallised. This was washed with water and ether.

Analysis: Found C = 47.47 H = 4.76

Calc. for $Ru(bipy)_2Cl_2\ H_2O$ C = 47.7 H = 4.77

Biscyanobis(bipyridyl)ruthenium(II)dihydrate,

$(Ru(bipy)_2(CN)_2)2H_2O$

$(Ru(bipy)_2Cl_2)$(.2 gms) in methanol (10 mls) and water (10 mls) was heated under reflux with excess potassium cyanide (1 gm). The initial purple brown solution soon turned bright orange. After one hour, the solution was filtered, and the methanol evaporated off on a water bath. On cooling bright orange crystals of $(Ru(bipy)_2(CN)_2)$ were deposited. These were washed with water, then recrystallised from methanol/ether.

Analysis: Found C = 52.58 H = 3.74

Calc. for $(Ru(bipy)_2(CN)_2)2H_2O$ C= 52.6 H = 3.99

The compound was a nonelectrolyte in methanol.

$$\Lambda_{25^oC} = 4.0 \text{ ohms}^{-1} \text{ moles}^{-1} \text{ cm}^2$$

Bis(nitrite)bis(bipyridyl)ruthenium(II)dihydrate,

$Ru(bipy)_2(NO_2)_2 2H_2O$

This was prepared by a method analogous to that used for $(Ru(bipy)_2(CN)_2)2H_2O$

Analysis: Found C = 44.50, H = 3.82

Calc.for $Ru(bipy)_2(NO_2)_2 2H_2O$ C = 44.3 H = 3.79.

The compound is a nonelectrolyte in methanol.

Λ_{25^oC} = 2.0 $ohms^{-1}$ $moles^{-1}$ cm^2.

Bis(thiocyanate)bis(bipyridyl)ruthenium(II),

$(Ru(bipy)_2(SCN)_2)$

$(Ru(bipy)_2Cl_2)$ (2 gms) in water (10 mls) and methanol (10 mls) was refluxed with excess potassium thiocyanate (1 gm) for two hours. The solution gradually darkened, and deep purple crystals were deposited. After cooling, the crystals were filtered off, and washed with water and ether. They were recrystallised from dichloromethane/ether.

Analysis: Found C = 50.36 H = 3.14

Calc.for $(Ru(bipy)_2(SCN)_2)$ C = 49.9 H = 3.02

Ethylenediaminebis(bipyridyl)ruthenium(II)diperchlorate,

$(Ru(bipy)_2en)(ClO_4)_2$

The compound was prepared by a method analogous to that used for the corresponding 1,10-phenanthroline complex.[19] It was precipitated as the perchlorate, and recrystallised from water.

Analysis: Found C = 39.16 H = 4.05

Calc.for $(Ru(bipy)_2en)(ClO_4)_2$ C = 39.2 H = 3.56

Diaminebis(bipyridyl)ruthenium(II)diperchloratetrihydrate,

$(Ru(bipy)_2(NH_3)_2)(ClO_4)_2 3H_2O$

The complex was prepared by a method similar to that used for the 1,10-phenanthroline complex[19]. $Ru(bipy)_2Cl_2$ (.2 gms) in methanol (10 mls) and water (5 mls) was heated with concentrated ammonia solution (2 mls ".880") on a water bath for one hour. The solution turned dark red. It was then filtered, and on the addition of sodium perchlorate, the required complex crystallised. The crystals were filtered, then washed with a small amount of water. They were recrystallised from methanol/ether.

Analysis: Found C = 34.19 H = 3.86

Calc.for $(Ru(bipy)_2(NH_3)_2)(ClO_4)_2 3H_2O$ C = 34.2 H = 3.99

Acetylacetonatobis(bipyridyl)ruthenium(II)chloride-trihydrate $(Ru(bipy)_2acac)Cl.3H_2O$

The complex was prepared by a method analogous to that used for the corresponding 1,10-phenanthroline complex.[19] It was recrystallised from methanol/ether.

Analysis: Found C = 49.56, H = 4.61

Calc.for $(Ru(bipy)_2acac)C13H_2O$ C = 49.7 H = 4.82

Oxalatobis(bipyridyl)ruthenium(II)tetrahydrate, $(Ru(bipy)_2C_2O_4)4H_2O$

The oxalate complex was prepared by a method analogous to that used for the corresponding 1,10-phenanthroline complex.[19]

Analysis: Found C = 46.28 H = 4.08

Calc.for $Ru(bipy)_2C_2O_4.4H_2O$ C = 46.05 H = 4.18

Bispyridinebis(bipyridyl)ruthenium(II)diperchlorate $(Ru(bipy)_2(py)_2)(ClO_4)_2$

$(Ru(bipy)_2(py)_2)Cl_2$ was prepared by a method used for the analogous orthophenanthroline complex.[20] The perchlorate was prepared by adding a concentrated aqueous solution of sodium perchlorate dropwise to

$(Ru(bipy)_2(py)_2)Cl_2$ in methanol. The precipitate was washed with a little water, then recrystallised from methanol/ether.

Analysis: Found C = 46.44 H = 3.67

Calc.for $(Ru(bipy)_2(py)_2)(ClO_4)_2$ C = 46.7 H = 3.36

Chloropyridinebis(bipyridyl)ruthenium(II)perchlorate-trihydrate, $(Ru(bipy)_2pyCl)ClO_4.3H_2O$

This was prepared by a method analogous to that used for the corresponding 1,10-phenanthroline complex[20].

Analysis: Found C = 43.10 H = 3.68

Calc.for $(Ru(bipy)_2py.Cl)ClO_4 3H_2O$ C = 43.05 H = 3.94

Conductivity in methanol Λ_{25^oC} = 110 $ohms^{-1}$ $moles^{-1}$ cm^2 indicating a 1:1 electrolyte.

Ruthenium III.

Bis-bipyridyl complexes

Diaquobis(bipyridyl)ruthenium(III)triperchloratedihydrate, $(Ru(bipy)_2(H_2O)_2)(ClO_4)_3.2H_2O$

A solution of $(Ru(bipy)_2Cl_2)$ (0.2 gm) in methanol (5 mls) and water (10 mls) was heated on a water bath with silvernitrate (1 gm) for half an hour. The precipitated silverchloride was filtered off and the solution heated a

further hour, until it was dark blue in colour and the methanol had evaporated. On addition of sodium perchlorate the required complex precipitated.

Analysis: Found C = 30.24 H = 2.77

Calc.for $(Ru(bipy)_2(H_2O)_2)(ClO_4)_3.2H_2O$ C = 30.6 H = 3.06.

Acetylacetonatobis(bipyridyl)ruthenium(III)diperchlorate-hydrate $(Ru(bipy)_2acac)(ClO_4)_2.H_2O$

$(Ru(bipy)_2acac)Cl$ (0.2 gms) was disolved in water (5 mls). A concentrated aqueous solution of ammonium ceric nitrate was added dropwise until the red colour disappeared and the solution was dark blue. On the addition of sodium perchlorate, dark blue $(Ru(bipy)_2acac)(ClO_4)_2.H_2O$ crystallised. This was washed with water and ether.

Analysis: Found C = 41.40 H = 3.48

Calc.for $(Ru(bipy)_2acac)(ClO_4)_2H_2O$ C = 41.10 H = 3.43.

Ruthenium.

Mono-bipyridyl complexes

These were all prepared by methods used by Dwyer et al.[18] The complex $(bipyH)(RubipyCl_4)$ was oxidised with chlorine to give the mono-complex $(Ru(bipy)Cl_4)$. This was then suspended in an aqueous alcoholic solution, and heated with the appropriate ligand to give the required complex.

The bromo complex, $K(Ru(bipy)Br_4)$ was prepared by heating $(Ru(bipy)Cl_4)$ with hydrobromic acid. The halo-complexes $(Ru(bipy)(py)_2X_2)$ were prepared by heating the tetrapyridine complex, $(Ru(bipy)(py)_4)(ClO_4)_2$ with the appropriate halide. The nonelectrolyte complexes soon precipitated. The trivalent complex, $(Ru(bipy)(py)_2Cl_2)ClO_4$ was prepared by oxidising the divalent complex with chlorine.

The analytical figures are tabulated below.

Compound	Found		Calculated Analyses	
	C%	H%	C%	H%
$K(RubipyCl_4)H_2O$	27.03	2.22	26.27	2.19
$K(RubipyBr_4)H_2O$	19.05	1.58	18.9	1.57
$(Ru(bipy)acac\ Cl_2)H_2O$	40.84	3.34	41.2	3.9
$(Ru(bipy)(acac)_2)Cl.3H_2O$	43.27	4.79	43.9	5.13
$(Ru(bipy)(py)_4)(ClO_4)_2$	46.55	4.29	46.6	3.63
$(Ru(bipy)(py)_2Cl_2)H_2O$	46.69	3.72	47.5	3.9
$(Ru(bipy)(py)_2Br_2)2H_2O$	38.76	3.20	39.2	3.6
$(Ru(bipy)(py)_2I_2)2H_2O$	33.97	2.57	33.97	3.1
$(Ru(bipy)(py)_2Cl_2)ClO_4 3H_2O$	37.65	3.73	37.4	3.74

Osmium (II)

Bis-bipyridyl complexes

Several of these were prepared by methods outlined by Buckingham et al.[29] These involved heating under reflux a solution of $(Os(bipy)_2Cl_2)$ with the appropriate ligand. The electrolyte complexes were isolated as the perchlorates.

Several new complexes were also prepared using similar methods.

The analytical figures for the complexes previously prepared are tabulated below.

Compound	Found			Calculated Analyses		
	C%	H%	N%	C%	H%	N%
$(Os(bipy)_2acac)Cl.2H_2O$	43.07	4.15	8.44	44.55	4.16	8.32
and	42.83	3.92	7.95			
$(Os(bipy)_2en)(ClO_4)_2$	34.45	3.88		34.3	3.15	
$(Os(bipy)_2(py)_2)(ClO_4)_2$	41.77	3.43	9.74	41.9	3.03	9.79
$(Os(bipy)_2C_2O_4)3H_2O$	41.16	3.95	8.80	41.0	3.42	8.70
	39.52	3.42	8.74			
$(Os(bipy)_2Cl_2)H_2O$	40.38	3.38	9.50	40.6	3.04	9.47
	39.82	3.42				
$(Os(bipy)_2phen)(ClO_4)_2.H_2O$	42.84	3.18	9.40	42.7	2.90	9.35
$(Os(bipy)_3)(ClO_4)_2.2H_2O$	40.22	3.14	9.42	40.3	3.14	9.41

Bis(thiocyanate)bis(bipyridyl)osmium(II)dihydrate,

$(Os(bipy)_2(SCN)_2)2H_2O$.

$(Os(bipy)_2Cl_2)$ (.2 gm) in water (10 mls) and ethanol (10 mls) was refluxed with excess potassium thiocyanate (1 gm) for twelve hours. A dark red precipitate slowly formed. The solution was filtered, and the complex washed with water, ethanol and ether.

It is only slightly soluble in alcohol and chloroform, but is soluble in dimethylformamide.

Analysis: Found C = 40.86 H = 3.22 N = 12.67

Calc.for $(Os(bipy)_2(SCN)_2)2H_2O$ C = 40.4 H = 3.06 N = 12.85.

Biscyanobis(bipyridyl)osmium(II)trihydrate,

$(Os(bipy)_2(CN)_2)3H_2O$

$(Os(bipy)_2Cl_2)$ in ethanol (10 mls) and water (10 mls) was refluxed with excess potassium cyanide for eight hours. The solution gradually turned brown. It was then filtered, and after evaporation of the ethanol on a water bath, the complex crystallised. It was washed with water, then recrystallised from methanol/ether.

Analysis: Found C = 43.15 H = 3.95 N = 13.07

Calc.for $(Os(bipy)_2(CN)_2)3H_2O$ C = 43.4 H = 3.62 N = 13.8

Conductivity in methanol indicated a nonelectrolyte.

Λ_{25^oC} = 1.8 $ohms^{-1}$ $moles^{-1}$ cm^2

Osmium (III).

The complexes were prepared by oxidation with chlorine of the corresponding divalent complexes.[29] They were isolated as the perchlorates. Analytical figures are tabulated below.

Compound	Calculated Analyses			Found		
	C%	H%	N%	C%	H%	N%
$(Os(bipy)_3)(ClO_4)_3$	35.6	2.97	8.32	35.69	2.98	8.30
$(Os(bipy)_2(py)_2)(ClO_4)_3$	37.56	2.64	8.76	37.41	2.88	8.79
$(Os(bipy)_2phen)(ClO_4)_3 3H_2O$	37.8	2.76		37.55	2.88	

Acetylacetonatobis(bipyridyl)osmium(III)diperchloratehydrate,

$(Os(bipy)_2acac)(ClO_4)_2.H_2O$

$(Os(bipy)_2acac)Cl$ (.2 gms) in water (5 mls) was oxidised with a saturated solution of ammonium ceric nitrate added dropwise. The colour changed from red to orange-brown. The complex was precipitated by adding sodium perchlorate, and washed with water and ether.

Analysis: Found C = 37.16 H = 3.61

Calc.for $(Os(bipy)_2acac)(ClO_4)_2H_2O$ C = 36.7 H = 3.13.

Osmium.

Mono-bipyridyl complexes

Tetrachlorobipyridylosmium(IV), $(OsbipyCl_4)$

$(bipyH_2)(OsCl_6)$ (1 gm) was pyrolysed in the manner described by Buckingham.[28] The brown residue was suspended in water (150 mls) and sodium dithionite (2 gms) added. The solution was filtered, and the residue again suspended in water, and dithionite added. The filtrates were oxidised with chlorine, and orange $OsbipyCl_4$ precipitated. This was washed with water and ether.

Potassiumtetrachlorobipyridylosmium(III)tetrahydrate,

$K(OsbipyCl_4)4H_2O$

The complex was prepared as described by Buckingham,[28] by reduction of the tetravalent complex, $(OsbipyCl_4)$ with hypophosphorous acid.

Analysis: Found C = 20.24 H = 2.94

Calc.for $K(OsbipyCl_4)4H_2O$ C = 20.20 H = 2.68.

Bisethylenediaminebipyridylosmium(II)diperchlorate

$(Os(bipy)(en)_2)(ClO_4)_2$

$(OsbipyCl_4)$ (0.2 gms) was suspended in ethanol (10 mls) and water (10 mls) and refluxed with ethylenediamine (0.5 mls) for twelve hours. The solution was filtered and

evaporated to dryness on the water bath. The residue was dissolved in water (5 mls) and the complex precipitated on the addition of sodium perchlorate. It was recrystallised from methanol/ether.

Analysis: Found C = 26.07 H = 3.75

Calc.for $(Osbipy(en)_2)(ClO_4)_2$ C = 27.23 H = 3.61

Bisacetylacetonatobipyridylosmium(III)perchloratetrihydrate,

$(Os(bipy)(acac)_2)ClO_4.3H_2O$

$(Os(bipy)Cl_4)$ (0.2 gms) was suspended in ethanol (10 mls) and water (10 mls) and refluxed with acetylacetone (0.5 mls) in the presence of calcium carbonate. After eight hours the solution was filtered, and $(Os(bipy)(acac)_2)ClO_4.3H_2O$ crystallised on the addition of sodium perchlorate.

Analysis: Found C = 33.01 H = 3.88

Calc.for $(Osbipy(acac)_2)ClO_4.3H_2O$ C = 33.98 H = 3.98

Tetrapyridinebipyridylosmium(II)diperchloratedihydrate

$(Os(bipy)(py)_4)(ClO_4)_2 2H_2O$

$(Os(bipy)Cl_4)$ in ethanol (10 mls) and water (10 mls) was heated on the water bath for one hour with pyridine (1 ml). The solution was evaporated to half volume, and extracted several times with dichloromethane to remove

brown $(Os(bipy)Cl_3py)$. This solution was evaporated to small volume, and $(Os(bipy)Cl_3py)$ precipitated on the addition of ether. This was then used to prepare the tetrapyridine complex as described by Buckingham.[28]

Analysis: Found N = 9.59

Calc.for $(Os(bipy)(py)_4)(ClO_4)_2.2H_2O$ N = 9.4

4,4'-dimethylbipyridyl complexes

The 4,4'-dimethylbipyridyl complexes were generally prepared by methods similar to those used for the corresponding unsubstituted bipyridyl complexes.

Iron.

Tris(4,4'-dimethylbipyridyl)iron(II)dichloridehexahydrate, $(Fe(4,4'\text{-diMebipy})_3)Cl_2.6H_2O$

The compound was prepared by adding a slight excess of 4,4'-dimethylbipyridine (0.56 gms) in 1 M hydrochloric acid (5 mls) to a solution of ferrous chloride (0.2 gms) in 1 M hydrochloric acid (3 mls). The required complex slowly crystallised on cooling. It was washed well with ether to remove any excess ligand. It could be recrystallised from water or from methanol/ether.

Analysis: Found C = 56.18 H = 6.39

Calc.for $(Fe(4,4'\text{-diMebipy})_3)Cl_2.6H_2O$ C = 56.2 H = 6.0

Biscyanobis(4,4'-dimethylbipyridyl)iron(II)chloroform,

$(Fe(4,4'\text{-diMebipy})_2(CN)_2)CHCl_3$

This compound was prepared by the method described by Schilt[5] for the unsubstituted bipyridyl complex. Excess potassium cyanide was added to an aqueous solution of the tris (4,4'-dimethylbipyridine) complex. The violet complex which precipitated on standing was recrystallised from chloroform. The N.M.R. spectrum of the complex in methanol indicated chloroform was present in the complex.

Analysis: Found C = 55.25 H = 5.31

Calc.for $(Fe(4,4'\text{-diMebipy})_2(CN)_2)CHCl_3$ C = 54.4 H = 4.2

Dipotassiumtetracyano4,4'-dimethylbipyridineiron(II)-tetrahydrate, $K_2(Fe(4,4'\text{-diMebipy})(CN)_4)4H_2O$

This compound was prepared by the method described by Schilt[5] for the unsubstituted bipyridyl. Excess potassium cyanide was added to an aqueous suspension of the bis complex, $(Fe(4,4'\text{-diMebipy})_2(CN)_2)$, and the solution heated on the water bath for about twelve hours. After filtration and the evaporation of excess solvent the complex crystallised. It was recrystallised from a small quantity of water.

Analysis: Found C = 38.89 H = 4.49

Calc.for $K_2(Fe(4,4'\text{-diMebipy})(CN)_4)4H_2O$ C = 38.9 H = 4.05

Ruthenium

Dichlorobis(4,4'-dimethylbipyridyl)ruthenium(II)hydrate, $(Ru(4,4'\text{-diMebipy})_2Cl_2)H_2O$

The complex $(4,4'\text{-diMebipyH})(Ru(4,4'\text{-diMebipy})Cl_4)$ was prepared from potassium pentachloroaquoruthenate, $K_2(RuCl_5H_2O)$ by the method used by Bosnich and Dwyer[20] for the analogous 1,10-phenantholine complex. This was converted to the bis-chloro complex $(Ru(4,4'\text{-diMebipy})_2Cl_2)$ by reduction with zinc as described for the corresponding unsubstituted bipyridyl complex (see page 29). It was recrystallised from dichloromethane/ether.

Analysis: Found C = 50.79 H = 4.72

Calc.for $(Ru(4,4'\text{-diMebipy})_2Cl_2)H_2O$ C = 51.6 H = 4.65

Several other 4,4'-dimethylbipyridyl complexes were prepared from the dichloro-complex by methods used for the corresponding unsubstituted bipyridyl complexes (see page 30). The analytical figures are tabulated below.

Compound	Found		Calculated Analyses	
	C%	H%	C%	H%
$(Ru(4,4'\text{-diMebipy})_2(CN)_2)4H_2O$	52.24	5.48	52.6	5.38
$(Ru(4,4'\text{-diMebipy})_2(NH_3)_2)(ClO_4)_2.2H_2O$	38.51	4.39	39.0	4.60
$(Ru(4,4'\text{-diMebipy})_2acac)Cl.2H_2O$	47.97	5.68	47.5	5.40
$(Ru(4,4'\text{-diMebipy})_2(NO_2)_2).H_2O$	50.14	4.32	49.75	4.50

Tris(4,4'-dimethylbipyridyl)ruthenium(II)diperchlorate-dihydrate, $(Ru(4,4'\text{-diMebipy})_3)(ClO_4)_2.2H_2O$

This complex was prepared by a method used by Dwyer et al[15] for the preparation of the unsubstituted bipyridyl complex. The ligand was heated under reflux with an aqueous alcoholic solution of potassium pentachloro-hydroxyruthenate $K_2(RuCl_5OH)$ and sodium hypophosphite. The complex was isolated as the diperchlorate. It was recrystallised from methanol/ether or from water.

Analysis: Found C = 48.11 H = 4.81

Calc.for $(Ru(4,4'\text{-diMebipy})_3)(ClO_4)_2 2H_2O$ C = 48.7 H = 4.5

Osmium.

Tris(4,4'-dimethylbipyridyl)osmium(II)diperchloratedihydrate, $(Os(4,4'\text{-diMebipy})_3)(ClO_4)_2.2H_2O$

This was prepared by the method described by Buckingham[30] for the unsubstituted bipyridyl complex. The bromo-complex, $K_2(OsBr_6)$ was heated under reflux with the ligand in dimethylformamide and later in aqueous dimethyl formamide. The complex was isolated as the diperchlorate, and was recrystallised from water.

Analysis: Found N = 8.38

Calc.for $(Os(4,4'\text{-diMebipy})_3)(ClO_4)_2.2H_2O$ N = 8.59

Tris(4,4'-dimethylbipyridyl)osmium(III)triperchlorate-trihydrate, $(Os(4,4'\text{-diMebipy})_3)(ClO_4)_3.3H_2O$

This was prepared by oxidation of an aqueous solution of the corresponding divalent complex, $(Os(4,4'\text{-diMebipy})_3)(ClO_4)_2$ with chlorine.[29] The complex crystallised on the addition of sodium perchlorate.

Analysis: Found C = 39.51 H = 4.07

Calc.for $(Os(4,4'\text{-diMebipy})_3)(ClO_4)_3.3H_2O$ C = 39.5 H = 3.84.

5. Other Ruthenium Complexes

Preparation of Potassium pentachloroaquoruthenate(III) $K_2(RuCl_5H_2O)$.

The pentachlorohydroxyruthenate (IV), $K_2(RuCl_5OH)$, can be prepared by Charronet's[49] method. The reduction of this compound with formaldehyde gives the pentachloroaquoruthenate, $K_2(RuCl_5H_2O)$ (see page 48). However, a simpler method giving the same product was developed, using the methods described for the preparation of Howe's salt and Miolotti's salt.[51]

Ruthenium trichloride (2.1 gm) was dissolved in concentrated hydrochloric acid (30 mls) and water (50 mls). Excess potassium chloride was then added, and the solution warmed for a few minutes on the water bath. Dark red crystals formed. These were filtered off and washed with a little water. The red crystals (0.6 g) were then dissolved in a solution of water (48 mls), ethanol (12 mls) and concentrated hydrochloric acid (1.5 mls). The solution was heated for two hours on the water bath. The colour changed from dark red to light orange. It was then set aside for two or three days, evaporated almost to dryness and allowed to crystallise. Red crystals of $K_2(RuCl_5H_2O)$

were obtained in high yield.

A Ruthenium Carbonyl Complex

The usual method of obtaining the pentachloroaquo-ruthenate (III), $K_2(RuCl_5H_2O)$ is by reducing an acidic (1 Molar HCl) solution of $K_2(RuCl_5OH)$ with formaldehyde. Often a red solution was produced from which $K_2(RuCl_5H_2O)$ crystallised. However, in some cases a blue green solution resulted. On crystallisation two compounds, one green, the other red, were obtained in varying proportions. The green complex was slightly more soluble in water than the red one, but the solution turned red on standing, and efforts to separate the two were unsuccessful. The infra red spectra of the red/green mixture and the red complex were very similar, both showing a broad band at approximately $1940cm^{-1}$. Repeated efforts to determine the factors leading to this complex in preference to $K_2(RuCl_5H_2O)$ were unsuccessful, although a high concentration of $K_2(RuCl_5OH)$ did seem to favour the formation of the complex with the infra red band at $1940cm^{-1}$. Occasionally another compound, almost identical to that described above, but with two sharp infra red bands at $1905cm^{-1}$ and $1925cm^{-1}$ was found.

When these complexes, showing an infra red band at $1940cm^{-1}$, were added to bipyridyl in one molar hydrochloric acid, orange crystals of two types - one needlelike, the

other almost cubic - were formed. Both had identical infra red spectra, with a band at 1920cm^{-1}.

Species which could give rise to the band at ~1940cm^{-1} include a metal hydride, coordinated molecular nitrogen, nitric oxide or carbon monoxide. On oxidation with ceric ions, the complexes gave an insoluble brown complex with a strong infra red band at 2041cm^{-1}. Hydride and nitrogen complexes would be unlikely to exist under such strong oxidising conditions. Coordinated nitric oxide in unlikely as at no stage in the preparation is there any source from which it can come. Also nitric oxide stretching frequencies in the infra red are generally lower than those observed.[50] A metal carbonyl appears most likely, especially as formaldehyde could act as a source of CO.

The complexes were difficult to obtain pure as the carbonyl derivatives were not easily separated from the usual products of the reactions, e.g. $K_2(RuCl_5H_2O)$ and $(bipyH)(Ru(bipy)Cl_4)$. Samples containing the maximum amount of carbonyl compound, as denoted by the intensity of the infra red band at 1920cm^{-1}, were studied. The infra red spectra also showed two bands at 1603cm^{-1} and 1582cm^{-1}. The first band is characteristic of coordinated bipyridyl, and the second is characteristic of the bipyridylinium cation, $(bipyH)^+$

The analytical figures were:

Carbon = 42.58%, Hydrogen = 3.29%, Nitrogen = 9.57% and 9.42%.

A possible formulation is $(bipyH)(Ru(bipy)COCl_3)$, which has the analytical composition:

Carbon = 43.0%, Hydrogen = 3.59%, Nitrogen = 9.55%.

The complex was converted to a potassium derivative of lesser purity by warming $(bipyH)(Ru(bipy)COCl_3)$ in water or dilute acid. After filtering, excess potassium chloride was added, and fine brown crystals formed. The infra red band at $1582cm^{-1}$ (indicative of $(bipyH)^+$) was not obviously visible. The analytical figures for this material were not consistent, and were high for the complex $K(Ru(bipy)COCl_3)$, perhaps indicating incomplete removal of the bipyridinium cation.

Carbon = 34.06% and 32.61%, Hydrogen = 2.76% and 2.50%.

Figures calculated for $K(Ru(bipy)COCl_3)$ are:

Carbon = 30.6%, Hydrogen = 1.85%.

It was also observed that when $(bipyH)(Ru(bipy)COCl_3)$ is heated in solution, an insoluble yellow compound is precipitated, indicating that interconversion of the cations is not necessarily the only reaction occurring. The insoluble yellow material has an infra red band at $1955cm^{-1}$.

The carbonyl ligand in all of these complexes is not easily removed. An infra red study indicated that it was not replaced by oxidation of the complexes with chlorine, or by heating the carbonyl complex in dimethyl-formamide, or by reaction with other strong ligands.

The complex $(bipyH)(RubipyCl_4)$ is an important starting material for other bipyridyl complexes of ruthenium. As discussed above, it can often be contaminated with some of the carbonyl complex if potassium pentachloroaquoruthenate (III) which has been prepared by reduction of the hydroxy-complex with formaldehyde is used in its preparation. The carbonyl complex cannot be removed by any simple crystallisation procedures and will be present in any complexes prepared from a contaminated sample.

For this reason the reduction of $K_2(RuCl_5OH)$ with formaldehyde to give $K_2(RuCl_5H_2O)$ is an unsatisfactory method, and the method described on page 47 is to be preferred.

CHAPTER II

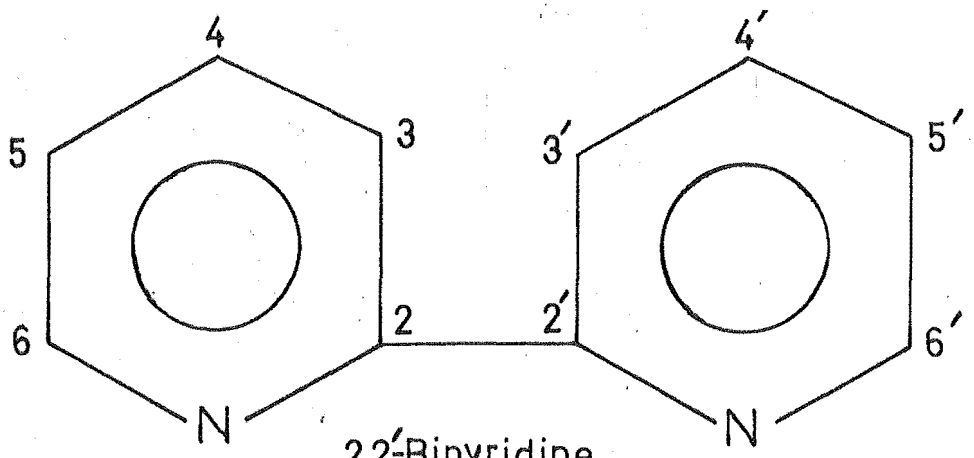
INTRODUCTION TO THE SPECTRA OF BIPYRIDYL COMPLEXES

INTRODUCTION

In this and the next two chapters the electronic absorption spectra of the bipyridyl complexes of divalent and trivalent iron, ruthenium and osmium are discussed. Where possible transitions have been assigned, but in some cases the data available has not enabled a definite assignment to the made. While it has been possible to correlate shifts in spectral bands with changes in the metal ion and/or coordinated ligands, a number of anomalous results become apparent in terms of our present understanding of charge transfer spectra.

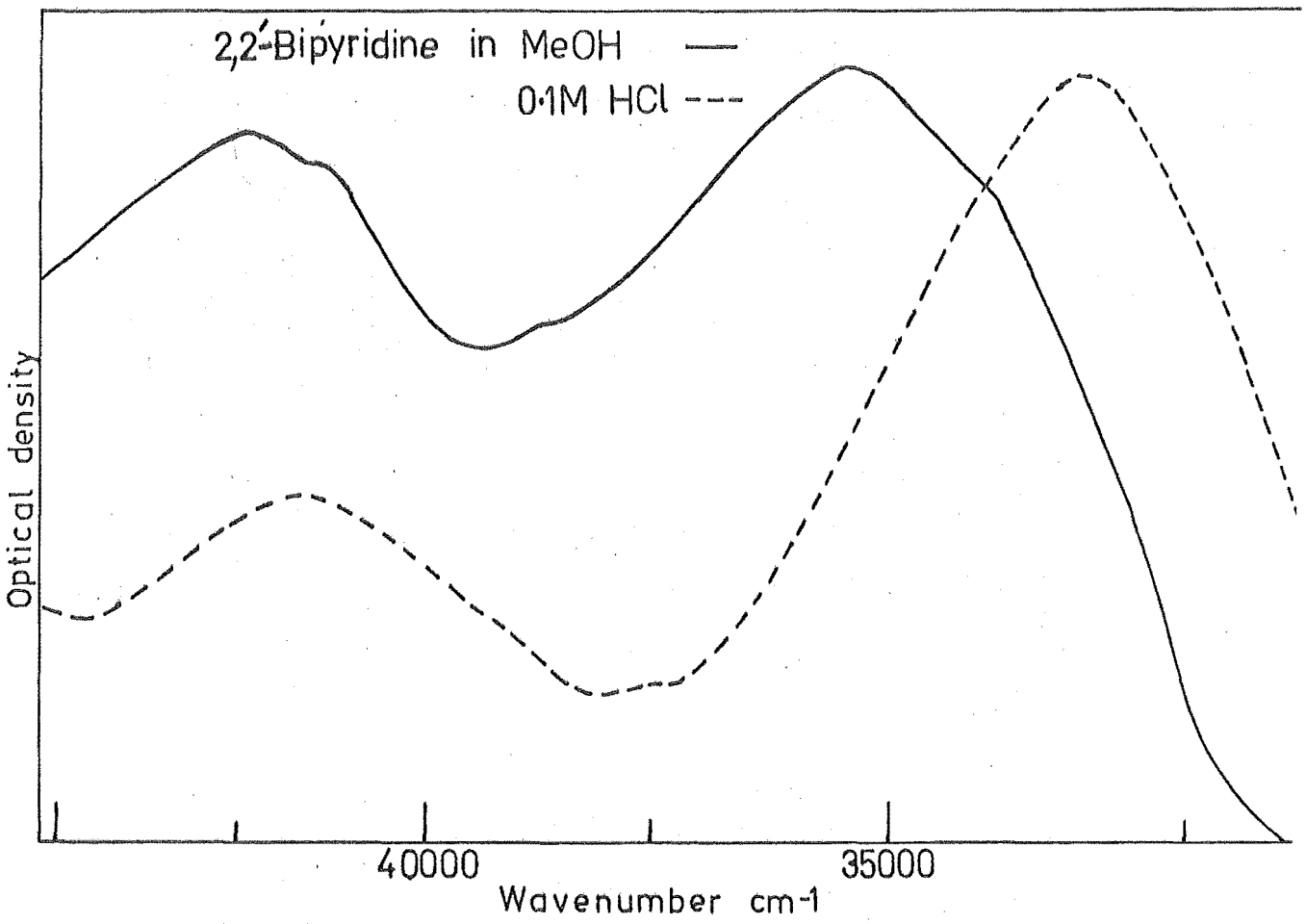
The spectra of the complexes are of two main types - intra-ligand spectra and charge transfer spectra. The intra-ligand spectra, present in all of the complexes, are bands, occurring in bipyridyl itself, which, on coordination of the bipyridyl to a metal ion are shifted, generally to lower energies. The charge transfer bands are those in which an electron is excited from an orbital, localised on the ligand to an orbital localised on the

FIGURE 1



2,2′-Bipyridine

FIGURE 2



metal (metal reduction spectra, present in the trivalent complexes) or the reverse (metal oxidation spectra present in the divalent complexes).

Molecular orbital theory, which considers the orbitals of both the metal and the ligands, must be used to give a theoretical understanding of such transitions. Because of the complexity of theoretical calculations for compounds of the type discussed in this work, the approach adopted here has been largely an empirical one. It was felt that by taking a wide range of closely related compounds it would be possible to obtain at least a qualitative description of the spectra. Any later theoretical approach would require a number of approximations and assumptions to be made, and this type of experimental method should help in making these.

THE BONDING OF BIPYRIDYL TO METAL IONS

Bipyridyl (see Fig.1) acts as a bidentate ligand and can form σ-donor bonds to a metal with the lone pairs on each of the nitrogen atoms in both the rings. It also has a set of filled orbitals of π-symmetry and a set of empty π^*-antibonding orbitals. The π^*-orbitals can be used for metal to ligand π-bonding, which is assumed to be an important component of the metal-bipyridyl bond in most

of the complexes.

The ultraviolet absorption spectrum of 2,2'-bipyridine in ethanol is shown in Fig.2. There are two main bands, one at 35,340cm^{-1} and one at 40,980cm^{-1}. The structure on the bands is assumed to be due largely to vibrational interactions.[52,53] In weakly acid solution a monoprotonated form exists, while in strong acid a diprotonated form is found. The spectra of these species are summarized below. (Extinction coefficients in parenthesis.)

Species	Solvent	Band Energies (cm^{-1}) I	Band Energies (cm^{-1}) II	Reference
bipy	Ethanol	35,340 (1.02×10^4)	40,980 (6.6×10^3)	54
$(bipyH)^+$	H_2O,pH=1.8	33,220 (7.8×10^3)	41,840 (3.7×10^3)	54
$(bipyH_2)^{2+}$	H_2O,pH=-.08	34,480	above 45,450	55

Unprotonated bipyridyl has a structure in which the ring nitrogens are trans to each other.[54,56,57] The monoprotonated form has the cis-configuration and forms hydrogen-bonds with the proton and the ring nitrogens while the diprotonated form reverts to the trans-configuration.

In a metal complex, bipyridyl must adopt the cis-configuration (when acting as a bidentate chelate) and in this situation it most closely parallels the monoprotonated

form. Gondo[52] predicted that in monoprotonated bipyridyl, the first excited state should have symmetry $^1B_1$ (37,100cm^{-1}) with a $^1A_1$ state at higher energy (38,200cm^{-1}). He also predicts a similar set of bands at 43,300cm^{-1} and 44,600cm^{-1}. The observed transitions have been assigned to the $^1B_1$ transitions as these are the more intense of the two.

Hanazaki and Nagakura[58] have carried out similar calculations, and obtained good agreement for the low energy bands, but not for the band at ~41,000cm^{-1}. Their calculations also indicated that the electron distribution is little different in the cis- and trans- forms of bipyridyl. These authors have also recently measured the ionization potentials of bipyridyl, but this work has not yet been published.

On coordination, the band at 35,340cm^{-1} in bipyridyl shifts, generally to lower energies. The band at 41,000cm^{-1} also shifts in most of the complexes, but in a less regular fashion. In some complexes it is not observed at energies below 45,450cm^{-1}, or may exist only as a shoulder on a strongly rising absorption.

Day and Sanders[60] from a consideration of simple molecular orbital theory for 1,10-phenanthroline complexes predicted that to a first approximation transitions involving orbitals of the 1,10-phenanthroline the total

dipole strength of the tris-complexes is three times, and that of the bis-complexes twice, that of a mono-complex. Qualitatively this trend in band intensities may be expected to hold, and indeed this was found to be the case. In the bipyridyl complexes studied in the present work, substitution of bipyridyl by other ligands led to a marked reduction in intensity of transitions involving the bipyridyl orbitals.

THEORETICAL STUDIES MADE ON BIPYRIDYL COMPLEXES

As mentioned previously, molecular orbital theory must be used to give the molecular energy levels necessary for understanding charge transfer spectra. It has been used for hexacyanide[61] and hexacarbonyl[62] complexes of transition metals, and also for many halogen complexes and oxyanions, e.g. 63. However, there are several difficulties associated with such calculations for bipyridyl complexes, often a consequence of the complexity of the ligand.

A knowledge of the molecular symmetry and bond lengths in a complex is desirable for any accurate molecular orbital calculations. However, there is little crystallographic data published for simple bipyridyl complexes. Estimations of bond lengths for osmium complexes, particularly osmium (II), are difficult since there is little

crystallographic data even for complexes not containing bipyridyl.

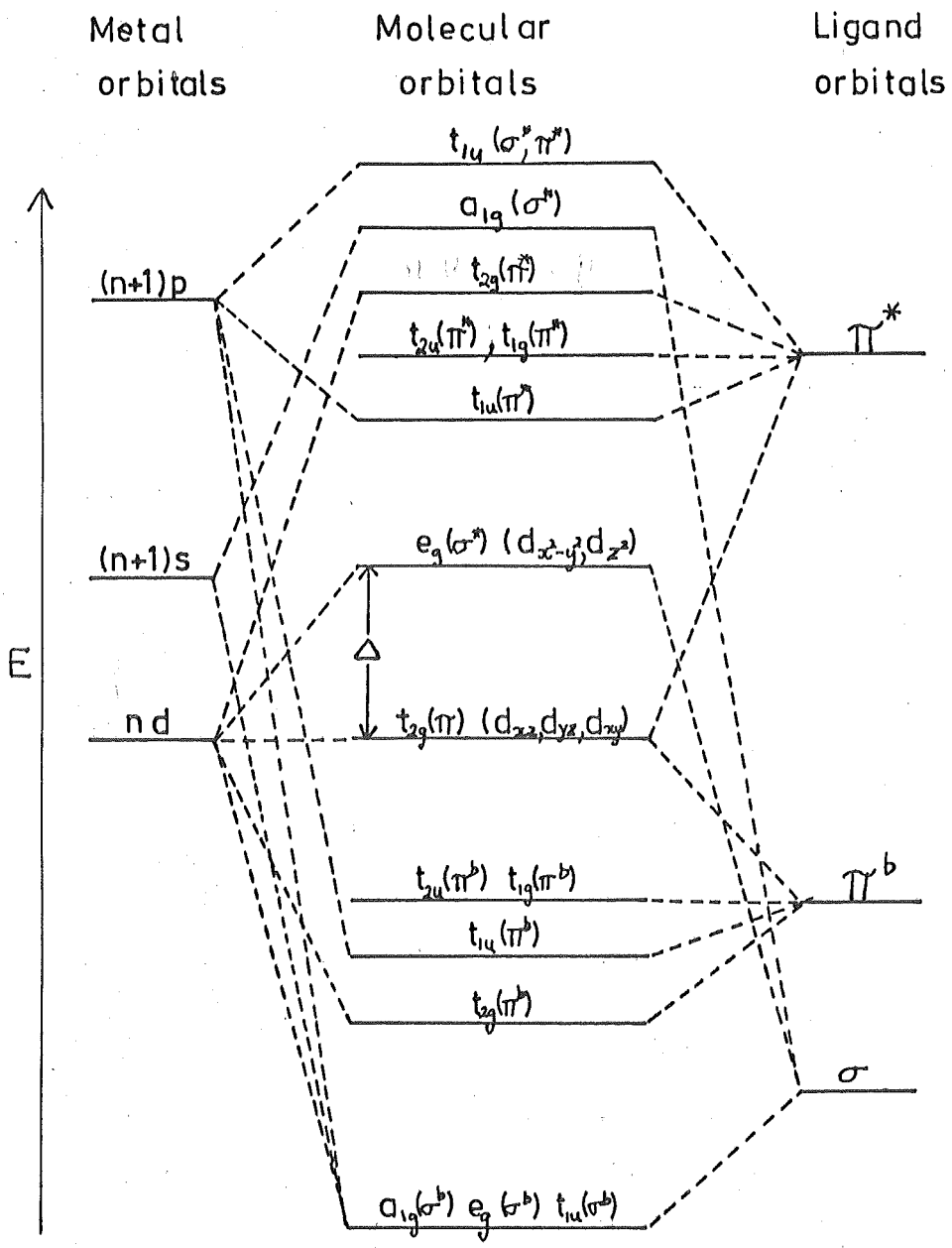
It is also necessary to have a good understanding of the energy levels in the free ligand (or in the case of bipyridyl the monoprotonated form) and although several calculations have been made[52,58] agreement between spectroscopic data and calculation is not always very good. Ionization potential data has now been measured for bipyridyl,[58] but is not yet published.

The symmetry of the complexes is always less than octahedral (see page 59) and this, as well as spin orbit coupling (see page 61) will give rise to added complications in any calculations.

However, several attempts at calculations have been made for the divalent iron complex, $(Fe(bipy)_3)^{2+}$ e.g.[58,59,64,65,66,67,68,69]. A recent calculation by Hanazaki and Nagakura[58] gives a good explanation of the spectrum of $(Fe(bipy)_3)^{2+}$.

In most cases, the symmetry of the complexes is assumed to be basically octahedral, an approximation which is quite reasonable for the tris complexes with six equivalent nitrogen atoms around the metal ion. It is also necessary to make an assumption of the value of the effective charge on the metal ion, though in some cases

FIGURE 3



Molecular orbital diagram for an octahedral complex containing π-bonding ligands.

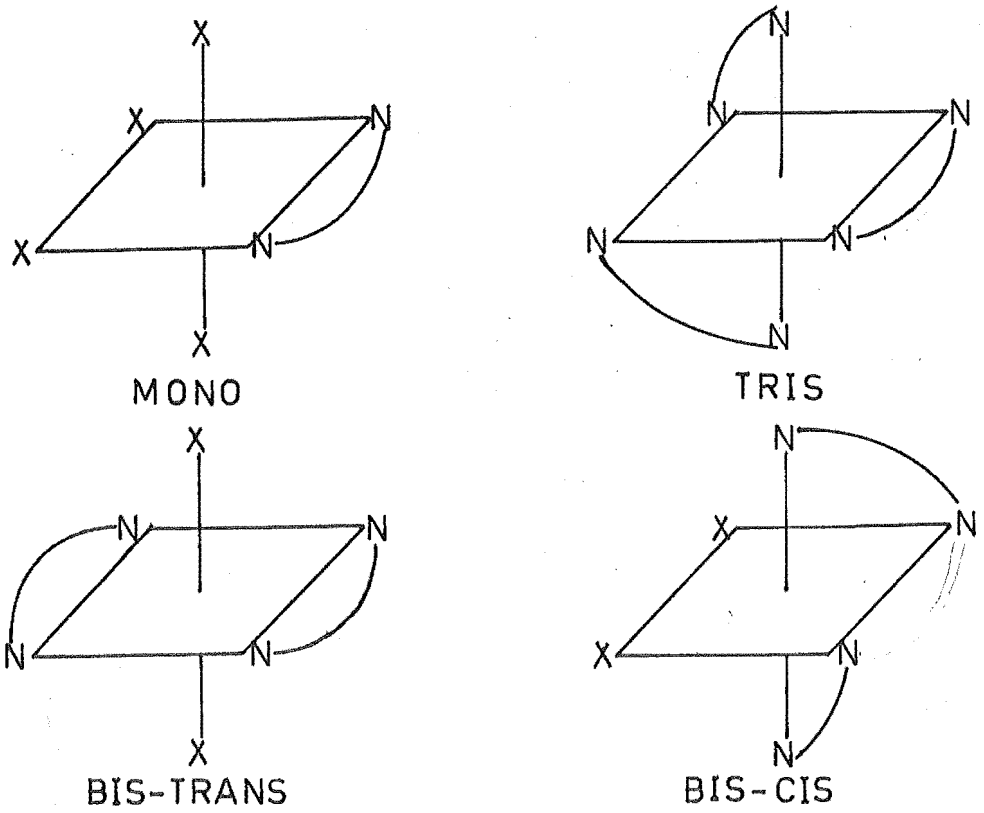
calculations have been made for several values of this figure. This effective charge is assumed to be localised on the σ-orbital system. The effect of the charge on the σ-system is then calculated, and since changes in the σ-system will affect the π-system, this effect is then calculated. Qualitative agreement has been found for some calculations. However, in many complexes, particularly the divalent ones, metal to ligand π-bonding is assumed to be of considerable importance, and most calculations take no account of this.

Studies of circular dichroism of bipyridyl complexes have also been carried out, and attempts have been made to assign the spectral bands, particularly the intra-ligand transitions.[53,70,71]

Although the discussion of the spectra of the complexes studied in this work is largely empirical, it is necessary to have at least a qualitative idea of the relative energy levels in the complexes. A molecular orbital scheme which has been found to be applicable to the hexacyanide complexes of the iron group is given in Fig.3. The relative order of the energy levels in probably very similar in the bipyridyl complexes.

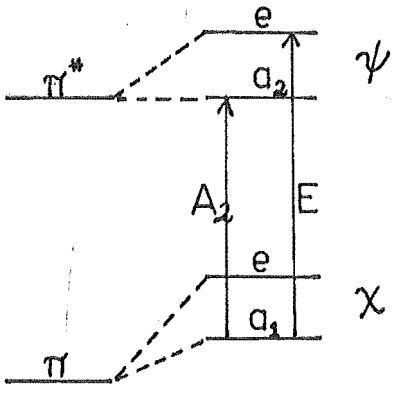
In the following discussion of the spectra of the bipyridyl complexes, the orbitals involved will be described in the terms applicable to octahedral symmetry - i.e. t_{2g}

FIGURE 4



Stereochemical configuration of bipyridyl complexes.

FIGURE 5



Possible splitting pattern for the π-orbitals in the tris-complexes.

and e_g will be used to describe the metal d-orbitals, although it is realized that this is only an approximation, and generally these orbitals will be split further by such things as spin orbit coupling and lower symmetry. Where the precise orbital involved in a transition is not known, it will be referred to as one of a group - e.g., ligand π-bonding orbital.

SYMMETRY OF THE COMPLEXES

In all of the complexes studied in this work the symmetry will be lower than octahedral. The tris-complexes, $(M(bipy)_3)^{n+}$ will have D_3 symmetry.

There are two possible isomers for the bis-bipyridyl complexes, $(M(bipy)_2X_2)^{n+}$. In the cis form the X groups are trans to a bipyridyl nitrogen, while in the trans form they are trans to each other. In the trans form, there would probably be considerable steric interaction between the C_6 hydrogen atoms of adjacent bipyridyl ligands. There has, as yet, been no conclusive evidence for the existence of any trans-bis-bipyridyl complexes. The bis-complexes discussed in this work almost certainly have the cis-configuration. Buckingham[30] has reported the resolution into optical isomers of the complex ion $(Os(bipy)_2(py)_2)^{2+}$ and several other related complexes. Resolution of the corresponding

ruthenium derivatives has also been accomplished.[23] Proton magnetic resonance data (Chapter VI) also establishes that several of the complexes are cis. Therefore these complexes will have symmetry C_2.

The mono-bipyridyl complexes, $(M(bipy)X_4)^{n+}$, will have symmetry C_{2v}. In both the mono-bipyridyl and the bis-bipyridyl complexes, the symmetry will be even lower when the other ligands coordinated besides bipyridyl are not all the same e.g. $(Ru(bipy)_2Clpy)^+$ symmetry C_s, and $(Ru(bipy)py_2Cl_2)$ symmetry C_s.

Orgel[72] has discussed the effect of D_3 symmetry in tris-bipyridyl complexes. The π-type orbitals of bipyridyl are classified as ψ (symmetric with respect to rotation about the C_2 symmetry axis) and χ (antisymmetric with respect to rotation about the C_2 axis). The ψ set span the A_2 and E representations of D_3, and the χ set and the metal "octahedral t_{2g} type" orbitals span A_1 and E. This can give rise to splitting of π- and π*- orbitals, and thus of the observed bands. A possible splitting pattern may be that shown in Fig.5 although the actual splitting pattern will be determined by the σ- and π- bonding in the complex, and the bands will probably overlap.

In C_2 and C_{2v} symmetry similar types of splittings are predicted. However, an examination of the band shapes in

the complexes studied in the present work indicates that there is little difference when the symmetry is altered provided the coordinated ligands are all close to each other in the spectro chemical series. The splitting of the bipyridyl π-orbitals appears to depend on the coordinated ligands, indicating that to a first approximation the same type of splitting occurs in all the complexes, regardless of their symmetry.

Nuclear magnetic resonance data (see Chapter VI) has shown that in the bis-bipyridyl complexes the two rings in the bipyridyl ligands had different electron distributions. This might be expected to cause some splitting of the spectral bands, but this is not observed, the bis-bipyridyl spectra being very similar to the tris-bipyridyl and mono-bipyridyl derivatives, and must therefore be small.

SPIN ORBIT COUPLING

Another effect which may cause further splitting of the bands is spin-orbit coupling. The effect would be small in the iron complexes, but would be much larger in the osmium complexes.[73]

$$\xi Fe \simeq 400$$

$$\xi Ru \simeq 1500$$

$$\xi Os \simeq 3000$$

In the trivalent complexes, the spectra of the iron

complexes are very similar to those of the corresponding ruthenium and osmium complexes, indicating that the effects are small. For a spin-paired d^5 complex, the ground state (assuming octahedral symmetry) would be split under spin orbit coupling. However if the splitting is large, then only the lower orbital will be occupied at low temperatures and provided the excited state is not split, no splitting will be observed.

The divalent d^6 spin-paired complexes will not be split in the ground state but the excited state may be split under spin-orbit coupling. The osmium complexes in this group all have much more complicated spectra in the visible region than the corresponding iron and ruthenium derivatives, and this could be a consequence of spin-orbit coupling.

It can therefore be seen that there are a considerable number of factors which could affect the spectra of the complexes. These will be discussed with particular reference to the divalent and trivalent bipyridyl complexes of iron, ruthenium and osmium in the next two chapters.

CHAPTER III

ELECTRONIC ABSORPTION SPECTRA OF COMPLEXES OF BIPYRIDYL WITH DIVALENT IRON, RUTHENIUM AND OSMIUM

INTRODUCTION

The numerical data for the electronic absorption spectra of the complexes of bipyridyl with divalent iron, ruthenium and osmium are given in Tables 2, 3 and 4. Diagrams of typical spectra are given in Figs.6-15. The complexes are of the type $(M(bipy)_3)^{2+}$, $(M(bipy)_2X_2)^{n+}$, $(M(bipy)_2XY)^{n+}$, $(M(bipy)X_4)^{n+}$, and $(M(bipy)X_2Y_2)^{n+}$, where X and Y include a wide range of ligands. In the following discussion, X and Y will generally be the ligands referred to as strong-field ligands or weak-field ligands.

All the complexes have similar ultraviolet spectra. They show two intense bands ($\varepsilon > 10^4$), one at ~33,000cm^{-1} and the other at ~41,000cm^{-1}, which are assigned to the intra-ligand transitions of bipyridyl. The visible spectra of the iron and ruthenium complexes show two intense bands ($\varepsilon > 10^3$) at ~20,000cm^{-1} and at ~27,000cm^{-1}. In complexes of ruthenium where X and Y are strong-field ligands the band at higher energy is not always resolved.

These bands are assigned to metal to bipyridyl charge transfer bands, although the high energy band may also have some other component.

The osmium compounds have much more complex visible spectra. They show several split bands in the visible, but these bands are also essentially metal to ligand charge transfer transitions.

The spectrum of the tris-bipyridyl complex of iron(II) $(Fe(bipy)_3)^{2+}$, has been studied by many authors, and the spectral bands have been assigned. e.g.[2,3,58,66,69,74,75,76] Several theoretical studies have been made for this complex.[58,59,64,65,66,67,68,69] There have also been several studies of the spectrum of the divalent ruthenium complex cation, $(Ru(bipy)_3)^{2+}$ e.g.[70,76] The spectrum of the osmium complex cation $(Os(bipy)_3)^{2+}$ has been reported.[30,78]

The visible spectra of the cyano-complexes of iron, $(Fe(bipy)_2(CN)_2)$ and $K_2(Fe(bipy)(CN)_4)$, have been reported, and the effect of concentration of added acid on the visible spectra studied.[5] The solid-state spectra of the ligand field bands of some spin-free bis-bipyridyl iron-(II) complexes have also been studied.[3]

The spectra of some bis-bipyridyl ruthenium(II) complexes have been reported,[21,22,77] but often the data are incomplete and the bands have not been assigned.

Buckingham[28,29,30] has published diagrams of the visible spectra of a few osmium complexes.

Mason et al[70] have recently published the spectra and circular dichroism of the tris-complexes of divalent iron, ruthenium and osmium.

FIGURE 6

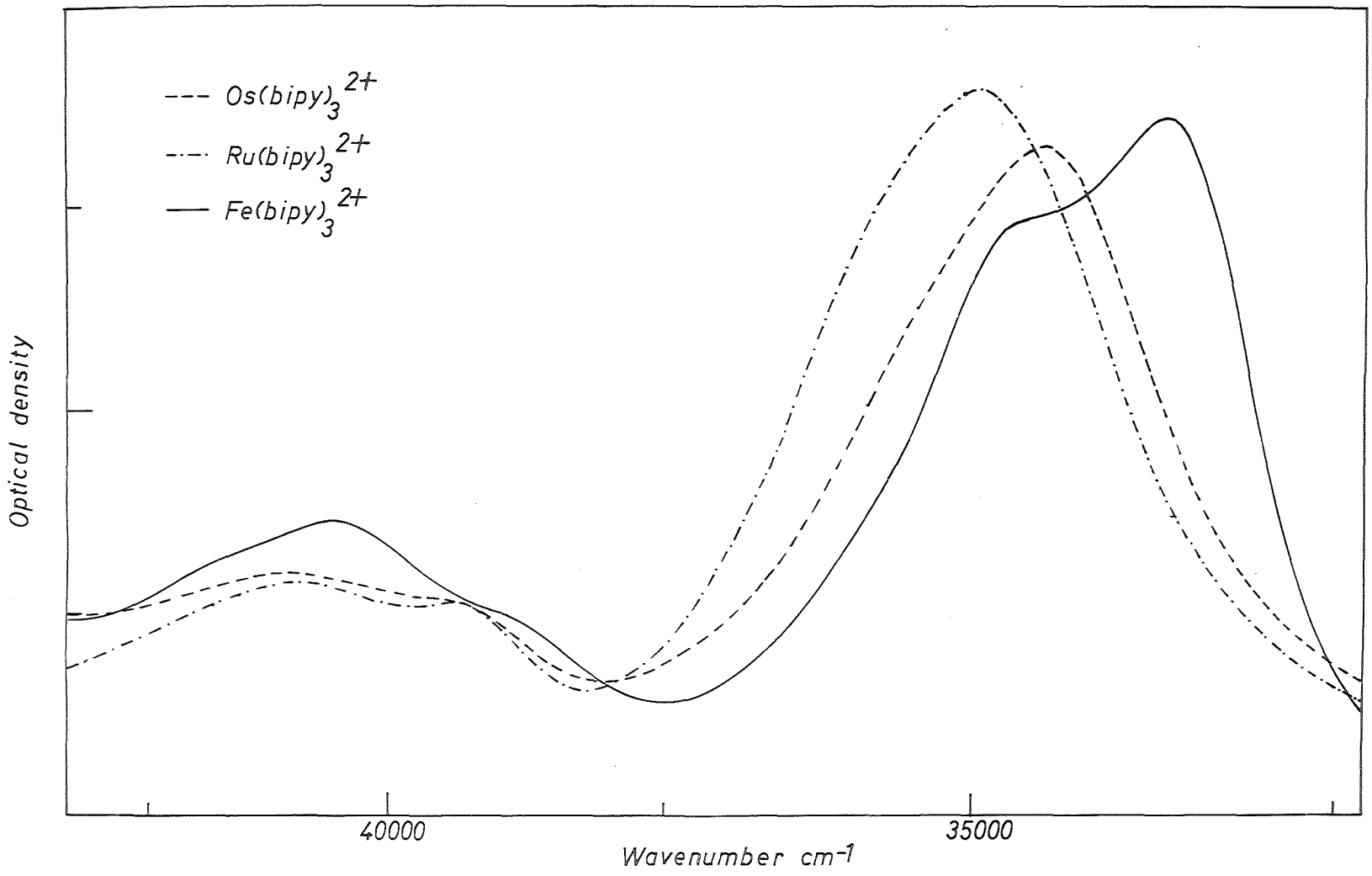
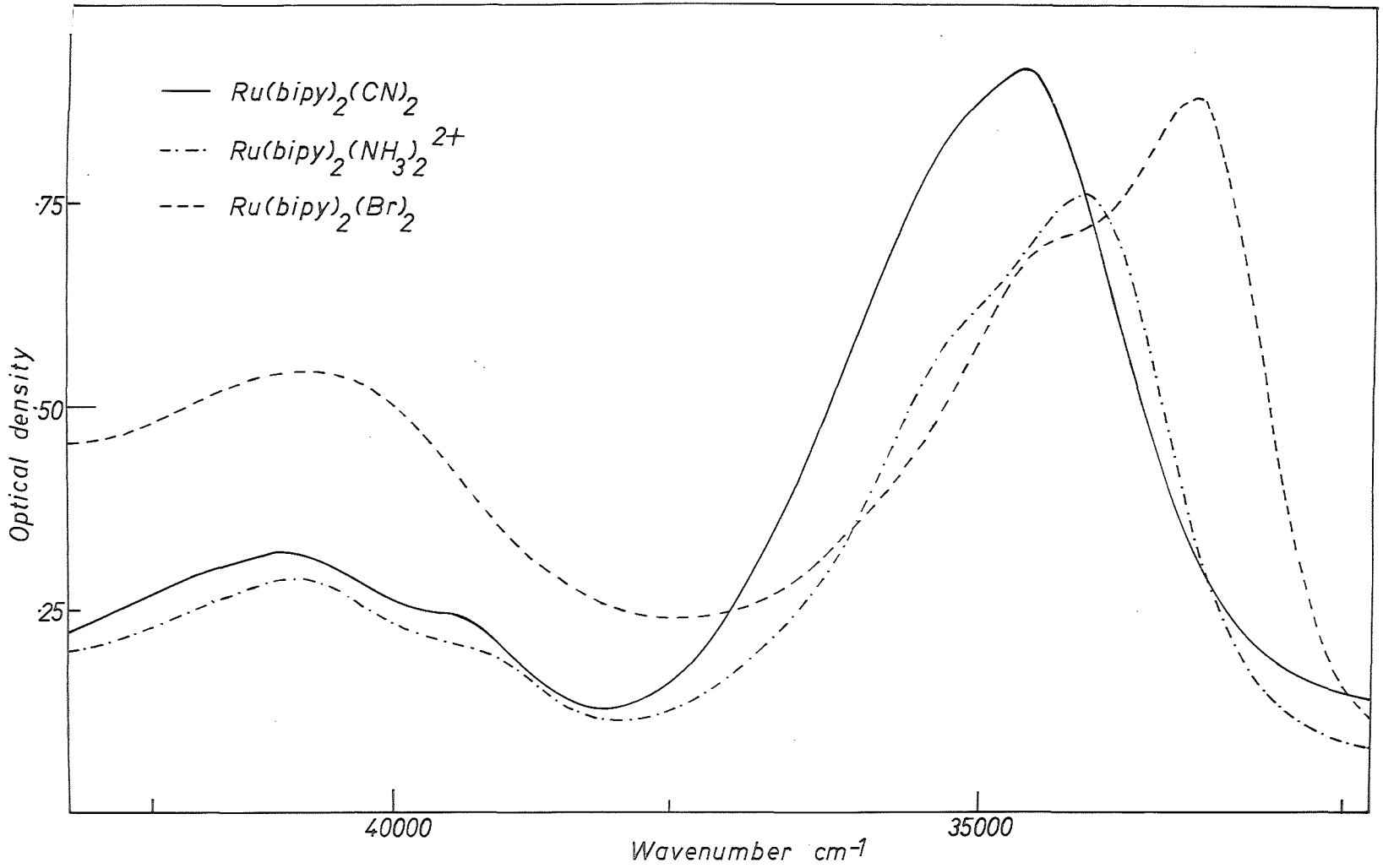

--- Os(bipy)3 2+
-·-· Ru(bipy)3 2+
—— Fe(bipy)3 2+
Optical density
40000
35000
Wavenumber cm-1

FIGURE 7


Ru(bipy)2(CN)2
Ru(bipy)2(NH3)2 2+
Ru(bipy)2(Br)2
·75
·50
·25
Optical density
40000
35000
Wavenumber cm-1

Intraligand Transitions

The band maxima for the intraligand transitions in the complexes are given in Table 5 and diagrams of typical spectra are given in Figs.6,7.

The complexes all show a band at ~33,000cm^{-1}, which has a prominent shoulder to lower energies in the iron complexes and in ruthenium complexes in which the coordinated ligands X and Y are weak-field ligands as in $(Ru(bipy)_2Cl_2)$. For all the osmium complexes and the ruthenium complexes containing strong field ligands X and Y as in $(Ru(bipy)_2(CN)_2)$, the shoulder is often not resolved and only a broadening of the higher energy side of the band is observed.

Most of the complexes also show a band at ~40,800cm^{-1}. This band has several shoulders to lower energies associated with it.

The bands have been assigned to $\pi \rightarrow \pi^*$ type transitions within the bipyridyl ligand by several authors, largely from studies of the tris-bipyridyl complexes of iron and ruthenium. e.g.[2,4,7,58,65,66,69,70,74,75,76,77] Similar transitions are observed in bipyridyl itself (see page 54), and the assignment is also in agreement with that predicted from theoretical calculations.[65,69,58] It has been observed in this work that the band at lower energy shows

a marked decrease in intensity as the number of coordinated bipyridyls is reduced from three to two to one.

Lower Energy $\pi \rightarrow \pi^*(1)$ Transition - Energy Trends.

The lower energy $\pi \rightarrow \pi^*(1)$ transition of bipyridyl (see page 54) is observed in bipyridyl complexes, and it is generally shifted to lower energies on coordination. A similar shift to lower energies is also observed in mono-protonated bipyridyl, which has the cis-configuration (see page 54). This shift in energy of the band has been considered to arise mainly from the effect of charge on the bipyridyl energy levels.[58,59,64,65,68,69] The trivalent complexes of iron, ruthenium and osmium of the $(M(bipy)_3)^{3+}$ group (see Chapter IV) all have this $\pi \rightarrow \pi^*(1)$ band at even lower energies than the corresponding divalent complexes. A similar shift to lower energies is also observed in the trivalent bipyridyl complexes of cobalt, rhodium and iridium.[79,80] These observations are consistent with the idea that charge is of primary importance in determining the energy of the $\pi \rightarrow \pi^*(1)$ separation. But other trivalent complexes e.g. $(Cr(bipy)_3)^{3+}$ (see Chapter V) and the trivalent bis-bipyridyl halogeno-osmium complexes e.g. $(Os(bipy)_2Cl_2)^{+}$ (see Chapter IV) have the intraligand band at energies very similar to that in free bipyridyl. Although metal ion charge may be of primary importance, it

is evident that other factors are also operating. It must also be remembered that the effective charge on the metal ion may be very different from the formal charge, and also that this effective charge may be very similar in the divalent and trivalent complexes.

The divalent bipyridyl complexes of iron, ruthenium and osmium, and to a lesser extent the trivalent complexes of the $(M(bipy)_3)^{3+}$ group (see Chapter IV), show a shift of the $\pi \rightarrow \pi^*(1)$ band to lower energies when the other coordinated ligands X and Y (besides bipyridyl) are weak field ligands. (see Table 5) Thus, as the average ligand field strength of the coordinated ligands around the metal increases, the energy of the $\pi \rightarrow \pi^*(1)$ transition increases. This increase in energy parallels that observed for the $t_{2g} \rightarrow \pi^*$ transition (see page 77) in the ruthenium complexes, though the energy change in the $\pi \rightarrow \pi^*(1)$ band as the ligands are changed is much smaller.

In the complexes $(M(bipy)_3)^{2+}$ and $(M(bipy)_2(CN)_2)$ where M = Fe, Ru, Os, (see Table 5) the energy of the $\pi \rightarrow \pi^*(1)$ transition increases in the order Fe < Os < Ru. In almost all the bipyridyl complexes, the energy of the transition is greater in the ruthenium complex than in the corresponding osmium complex.

The ligand field splitting, Δ, is generally greater for 5d complexes than for 4d ones. If the ligand field

splitting is important in determining the energy separation of the π- and π*- levels, as appears to be the case when changes in the coordinated ligands X and Y in a series are considered, and if Δ(Os) > Δ(Ru) then the transition would be expected to be at higher energies in osmium complexes than in ruthenium ones. This is not the order which is observed. However, for complexes containing strongly π-bonding ligands there is often little change in Δ for a series 3d→4d→5d,[61,62,81] and Δ(Os) may not be much greater than Δ(Ru).

Another factor which could be of importance in determining the energy of the π→π* transition is the relative energy of the t_{2g} metal orbital in the complexes as it has been shown, [e.g.72] (see page 60) that the metal t_{2g} type orbitals can combine with the ligand π- and π*-orbitals.

In the hexacyanide complexes of the iron group, $(M(CN)_6)^{4-}$,[81] a consideration of the energy of the first metal to ligand (t_{2g}→ligand) transition indicates that the energy of the t_{2g} level increases in the order Ru < Os < Fe. This stabilization of the t_{2g} orbitals in ruthenium and osmium is assumed to be a consequence of strong metal to ligand π-bonding. Bipyridyl is very similar to the cyanide ion in that it can also form strong π-bonds, and from studies of a similar transition (t_{2g}→π*(1), see page 75)

in the bipyridyl complexes it is known that the t_{2g} level in the cation $(Ru(bipy)_3)^{2+}$ is at lower energy than in the cation $(Fe(bipy)_3)^{2+}$. Unfortunately the corresponding $t_{2g} \rightarrow \pi^*$ transition in the osmium complexes cannot be unambiguously assigned.

Now the energy of the $\pi \rightarrow \pi^*(1)$ transition increases in the order Fe < Os < Ru. Therefore it seems that the higher the energy of the t_{2g} orbital the lower the energy of the $\pi \rightarrow \pi^*(1)$ transition. In a metal ion series, the strong field ligand X and Y will tend to lower the energy of the t_{2g} orbital (see page 77), and in these complexes e.g. in $(Ru(bipy)_2(CN)_2)$ the $\pi \rightarrow \pi^*(1)$ transition is at higher energy than in the complexes where the t_{2g} level is at higher energy e.g. in $(Ru(bipy)_2Cl_2)$, (see Table 5).

Both the ligand field parameters and the energy of the t_{2g} orbital are determined by a large number of factors, including metal ion charge, σ-bonding, π-bonding, size of metal ion etc. Although the energy of the $\pi \rightarrow \pi^*(1)$ transition does seem to be related to the energy of the t_{2g} level, this is probably not the only important factor. Charge is likely to be of primary importance, and there are probably other factors which have not yet been considered, as similar correlations do not always apply to other groups of compounds (see Chapter VI), and more work remains to be done.

The spin-free iron complexes, $(Fe(bipy)_2Cl_2)$, $(Fe(bipy)_2C_2O_4)$ do not fit into the same series as the ruthenium and osmium complexes, the $\pi\rightarrow\pi^*(1)$ transition being at higher energies in these complexes than for the diamagnetic tris complex cation $(Fe(bipy)_3)^{2+}$. However electron repulsion parameters will be different in these complexes from those in spin-paired complexes, and the presence of only four electrons in the t_{2g} orbitals could cause significant differences in both σ- and π- bonding. The screening of the metal ion charge will also be much more effective in these complexes than in the spin-paired ones.

Lower Energy $\pi\rightarrow\pi^*(1)$ Transition - Band Structure.

The structure on the band in bipyridyl itself and in some of its complexes has been ascribed to vibrational effects.[53,58,76,82] The splitting is much better resolved at low temperatures for $(Fe(bipy)_3)^{2+}$ and $(Ru(bipy)_3)^{2+}$.

In the complexes studied in the present work, all the iron complexes and those ruthenium complexes which contain weak field ligands X and Y e.g. $(Ru(bipy)_2Cl_2)$, show a prominent shoulder to higher energies on the $\pi\rightarrow\pi^*$ band, the actual splitting becoming less as X and Y become stronger ligands. (see Figs.6 and 7) In the ruthenium complexes with strong field ligands and in all the osmium complexes,

the splitting is much less, only a broadening of the higher energy side of the band being observed. In the ruthenium complexes, these changes in band shape are paralleled by changes in band shape of the $t_{2g} \rightarrow \pi^*(1)$ transition (see page 75) suggesting that it may be a splitting of the π^* orbitals which is causing these effects. In the iron and ruthenium complexes the splitting seemed to be related to the energy of the band - the higher the energy, the less the splitting. The osmium complexes however, have the band at lower energies than the ruthenium ones but show much less splitting. Generally, if the ligand field splitting in osmium is assumed to be greater than that in ruthenium, then the splitting may be said decrease as the average ligand field strength of the complex increases.

Orgel[72] (see page 60) and Ferguson[71] have discussed the interaction of the metal t_{2g} orbitals with the π-orbitals of the ligand, and suggested this can give rise to splitting in the $\pi \rightarrow \pi^*(1)$ transition since there are two possible transitions. In view of the regularity of the changes in band shape with coordinated ligand, and the large changes in the separation of the main band and shoulder (changes much greater than any in bands in the infra-red spectra of the complexes) suggest that vibrational effects are probably not the sole cause of the splitting. However,

as Ferguson[71] has pointed out, vibrational effects can radically alter the shapes of bands. But it seems likely that splittings of the electronic levels similar to those described by Orgel probably do have a considerable effect on the $\pi \rightarrow \pi^*(1)$ transition.

High Energy $\pi \rightarrow \pi^*(2)$ Transition.

The shifts in the energy of the high energy intraligand transition of the bipyridyl complexes are much less regular than those of the high energy band. No correlation of its energy with metal ion or ligand was found.

Hanazaki and Nagakura[58] have assigned this band in the cation $(Fe(bipy)_3)^{2+}$ to a $\pi \rightarrow \pi^*$ ligand transition and a third set of $t_{2g} \rightarrow \pi^*$ metal-oxidation bands. However, the present work can give no evidence for any definite assignments, and no separation of two sets of transitions (the intraligand bands and the charge transfer bands) was observed as the ligands X and Y were changed.

Other Expected Transitions.

In most complexes of pyridine with transition metals a strong absorption is present in the ultraviolet spectrum at ~38,500cm^{-1}. e.g.[3] This is assigned to an intraligand transition in the pyridine, similar to that observed in

bipyridyl complexes. However in the trivalent and divalent complexes containing both bipyridyl and pyridine, the pyridine intraligand transition is not observed. This may be due to it being hidden under a more intense bipyridyl transition, but this seems unlikely as the spectra of the complexes containing pyridine are very similar to the tris-bipyridyl complexes and show a marked decrease in intensity as the number of coordinated pyridines increase. Also in the region where the pyridine absorption would be expected to occur, the actual absorption is low.

Other complexes e.g. thiocyanato- or acetyl-acetonato- derivatives, which would also be expected to have intraligand bands in this region do not show these absorptions. The reason for these absences is not understood.

FIGURE 8

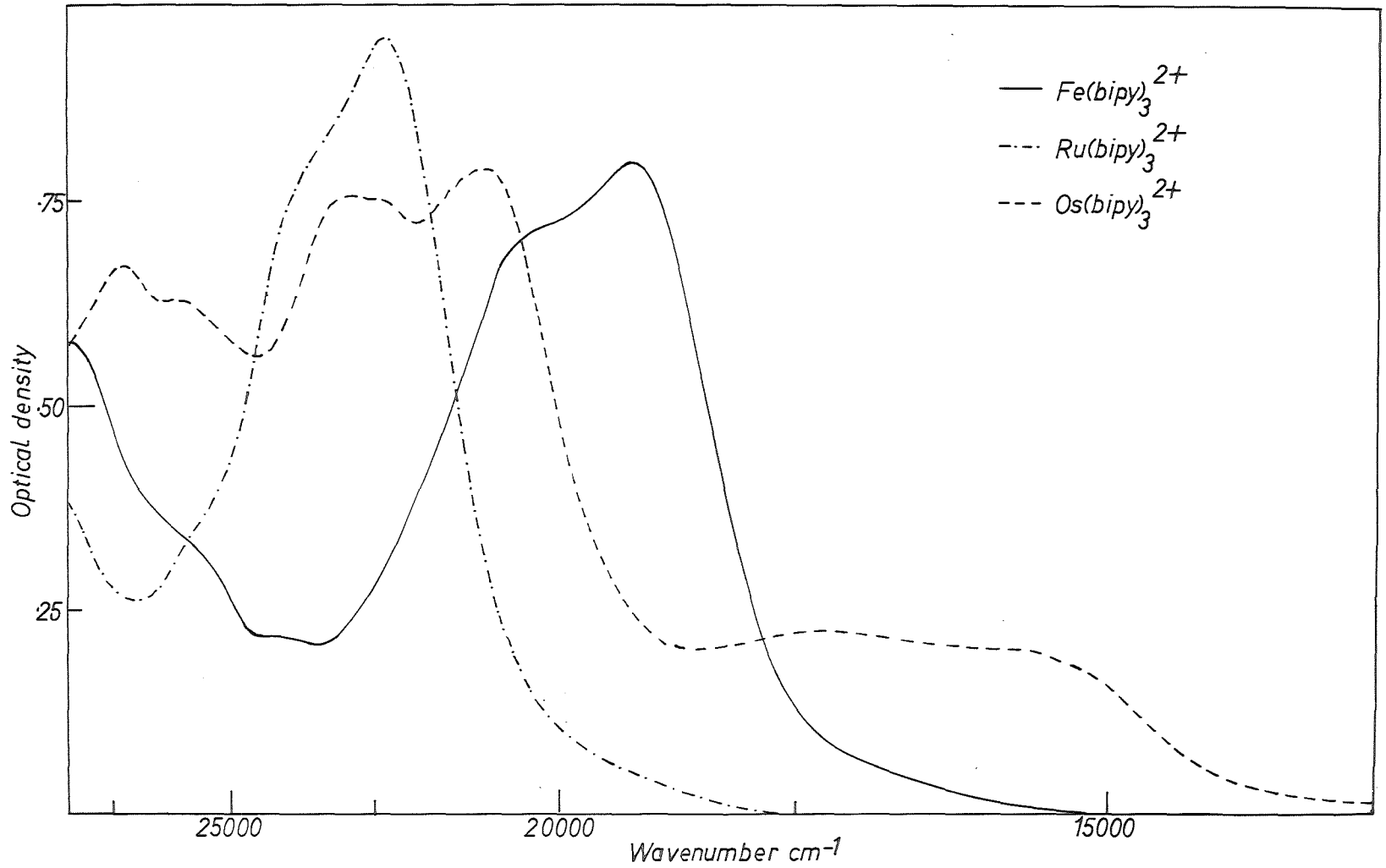
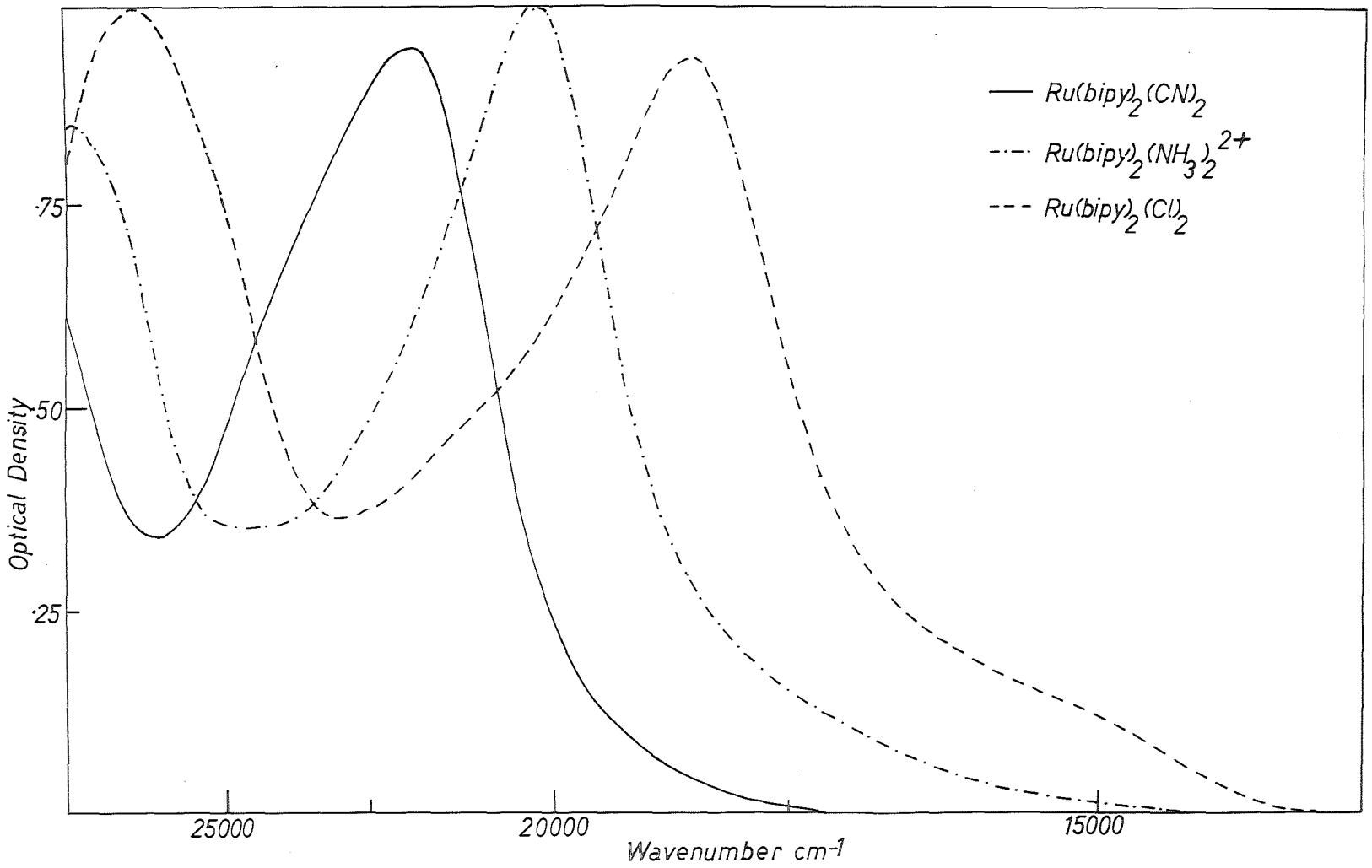

Fe(bipy)3 2+
Ru(bipy)3 2+
Os(bipy)3 2+
Optical density
·75
·50
·25
25000
20000
15000
Wavenumber cm-1

FIGURE 9


Ru(bipy)2(CN)2
Ru(bipy)2(NH3)2 2+
Ru(bipy)2(Cl)2
Optical Density
·75
·50
·25
25000
20000
15000
Wavenumber cm-1

Visible Spectra of the Divalent Iron and Ruthenium Complexes

Numerical data for the spectra of the complexes of iron(II) and ruthenium(II) with bipyridyl are given in Tables 2 and 3. Diagrams of typical spectra are given in Figs.8-12. A summary of the band energies for the complexes is given in Table 6.

The spectra generally show two bands of similar intensities at ~27,000cm^{-1} and at ~20,000cm^{-1}. There are also several shoulders on the bands, one of the more prominent being a shoulder to higher energy on the band at ~20,000cm^{-1} in the iron complexes and in ruthenium complexes containing coordinate ligands X and Y which are weak field ligands as in $(Ru(bipy)_2Cl_2)$. In ruthenium complexes where X and Y are strong field ligands as in $(Ru(bipy)_2(CN)_2)$, only a broadening of the band to higher energies is observed.

In complexes of ruthenium where X and Y are weak field ligands, another shoulder at lower energies (~17,000cm^{-1}) is also observed.

Lower Energy $t_{2g} \rightarrow \pi^*(1)$ Transition.

The band at ~20,000 cm^{-1} in the iron cation,

$(Fe(bipy)_3)^{2+}$, has been assigned by Krumholz[5] to a metal to ligand charge transfer band.

The metal electron must be one from the t_{2g} level, and the ligand orbital is one of the empty π-antibonding orbitals of the bipyridyl.

Williams[75,44] studied the effect of substituents on the energy of the band in the tris complexes of iron with substituted bipyridyls and 1,10-phenanthrolines. He found that electron-donating substituents e.g. methyl, cause a shift to lower energies relative to the unsubstituted ligand as expected for a metal-oxidation transition. These observations are consistent with the results obtained by Day and Sanders[59] in a theoretical study of similar complexes. Electron-donating substituents would tend to reduce the metal to ligand π-bonding, destabilising the metal t_{2g} orbital. This will lower the energy of a transition from the metal t_{2g} level to the π*-bipyridyl orbital. A shift in the opposite direction would be expected if the transition was of a metal-reduction type (as found for the trivalent compounds, see page 96).

Studies at low temperature by Palmer and Piper[76] showed that the bands in the cations $(Fe(bipy)_3)^{2+}$ and $(Ru(bipy)_3)^{2+}$ increased in intensity on cooling, as expected for charge transfer bands. A recent theoretical

study of the spectrum of the iron cation, $(Fe(bipy)_3)^{2+}$ by Hanazaki and Nagakura[58] also led to the assignment of the band to a metal-oxidation ($t_{2g} \rightarrow \pi^*$) transition.

In the course of the present work it was also found that the band intensity decreased as the number of coordinated bipyridyls decreased, indicating that orbitals in the bipyridyl ligand are involved in the transition.

The structure on the bands has been assigned to vibrational effects by several authors.[5,76,59] The splitting is very similar to that observed in the $\pi \rightarrow \pi^*$ transition and may also be a consequence of electronic effects as well as vibrational ones as discussed on page 70.

A wide range of ruthenium complexes were studied in the present work, and it was observed that this $t_{2g} \rightarrow \pi^*(1)$ band shifts to lower energy as the average ligand field strength of the coordinated ligands decreases (i.e. as X and Y become weak field ligands)(see Table 6). This shift can be correlated with the π-bonding ability of the ligands X and Y. Strongly π-bonding ligands e.g. CN^- in $(Ru(bipy)_2(CN)_2)$, will stabilise the t_{2g} level, thus increasing the energy of the $t_{2g} \rightarrow \pi^*$ transition. The observed shifts are in the same direction as those in the low energy $\pi \rightarrow \pi^*(1)$ transition (see page 68) but are much larger. This indicates that the change is one in the energy

of the t_{2g} orbitals, although the change in the energy of the π^*-orbital may increase the effect.

The changes in band energy as the ligands X and Y are changed in the iron compounds is somewhat more complex. In the case of the chloro-complex, $(Fe(bipy)_2Cl_2)$ and the oxalato-complex $(Fe(bipy)_2C_2O_4)$ this is probably a result of the complexes not being spin-paired. This will alter the σ-bonding, the π-bonding, the interelectronic repulsion terms, and the screening of the metal ion charge will also be more effective and the compounds cannot be compared with similar spin-paired ones.

In the tris-complexes $(M(bipy)_3)^{2+}$ and the cyano-complexes $(M(bipy)_2(CN)_2)$ the energy of the $t_{2g} \rightarrow \pi^*(1)$ transition is much higher in the ruthenium complexes than in the iron complexes. Normally the energy of the t_{2g} orbital would be expected to increase in the order 3d<4d<5d, as is observed in ammonia, aquo- and halogeno-complexes. However Gray and Beach[81] in a study of the divalent hexacyanide complexes $(M(CN)_6)^{4-}$ M = Fe, Ru, Os found the energy of the first metal to ligand transition increased in the order Fe<Os<Ru. They relate this to the effect of strong metal to ligand π-bonding. Ruthenium can form stronger π-bonds than iron, thus stabilising the t_{2g} orbital and increasing the energy of the $t_{2g} \rightarrow \pi^*$ transition.

Strong π-bonding in the bipyridyl complexes would have the same effect.

High Energy $t_{2g} \rightarrow \pi^*(2)$ Transition

In all the divalent complexes of iron and ruthenium except those of ruthenium which contain strong field ligands X and Y, as for $(Ru(bipy)_2(NO_2)_2)$ and $(Ru(bipy)_3)^{2+}$, there is also an intense band at ~27,000cm^{-1} which is broader than the lower energy band ($\delta \simeq 3000cm^{-1}$). The changes in band position with changes in solvent (see page 83), ligands and metal ion are very similar to those observed in the lower energy $t_{2g} \rightarrow \pi^*(1)$ transition just discussed, i.e. electron-donating substituents in the bipyridyl cause a shift to lower energies, and the inclusion of strong field ligands X and Y in the coordination sphere causes a shift to higher energies.

In the ruthenium complexes containing strong field ligands there are several shoulders observed between 27,000cm^{-1} and 30,000cm^{-1}, and the band, which would be expected to be at higher energies in these complexes than in those containing weak field ligands X and Y, could be concealed by the intense $\pi \rightarrow \pi^*(1)$ transition at ~34,000cm^{-1}. Further evidence for this is seen in the solvent effects

FIGURE 10

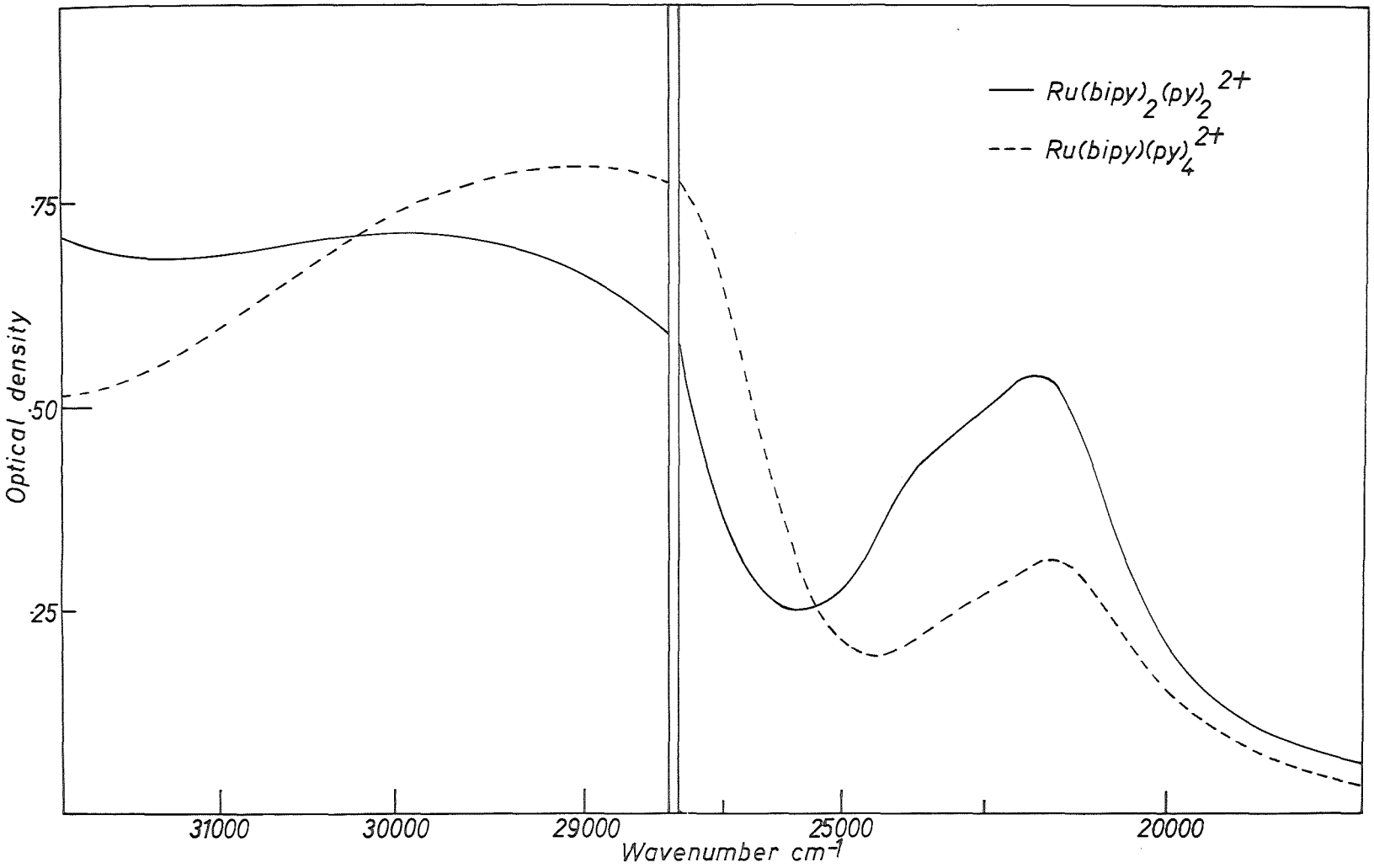

Ru(bipy)2(py)2 2+
Ru(bipy)(py)4 2+
Optical density
.75
.50
.25
31000
30000
29000
25000
20000
Wavenumber cm-1

FIGURE 11

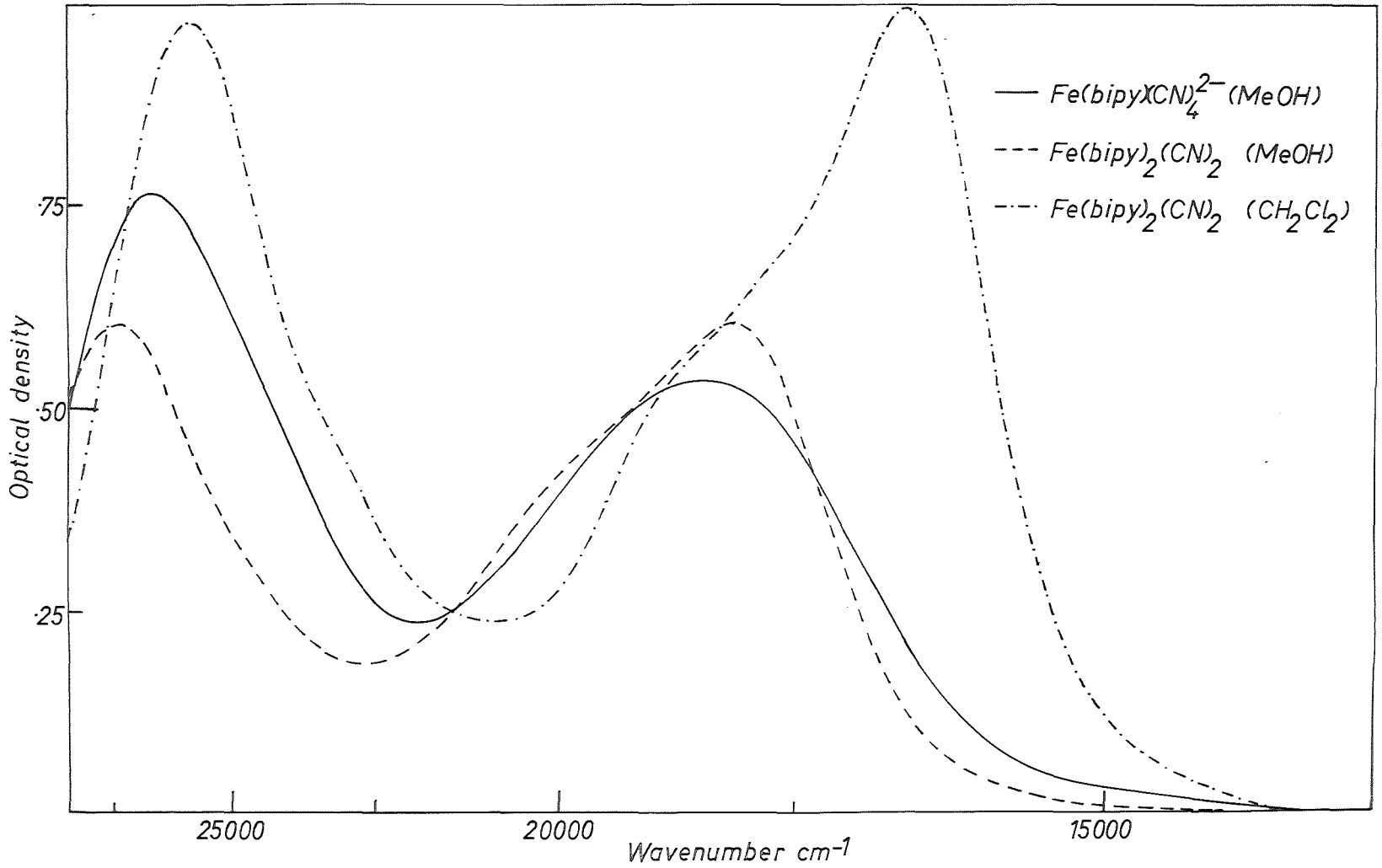
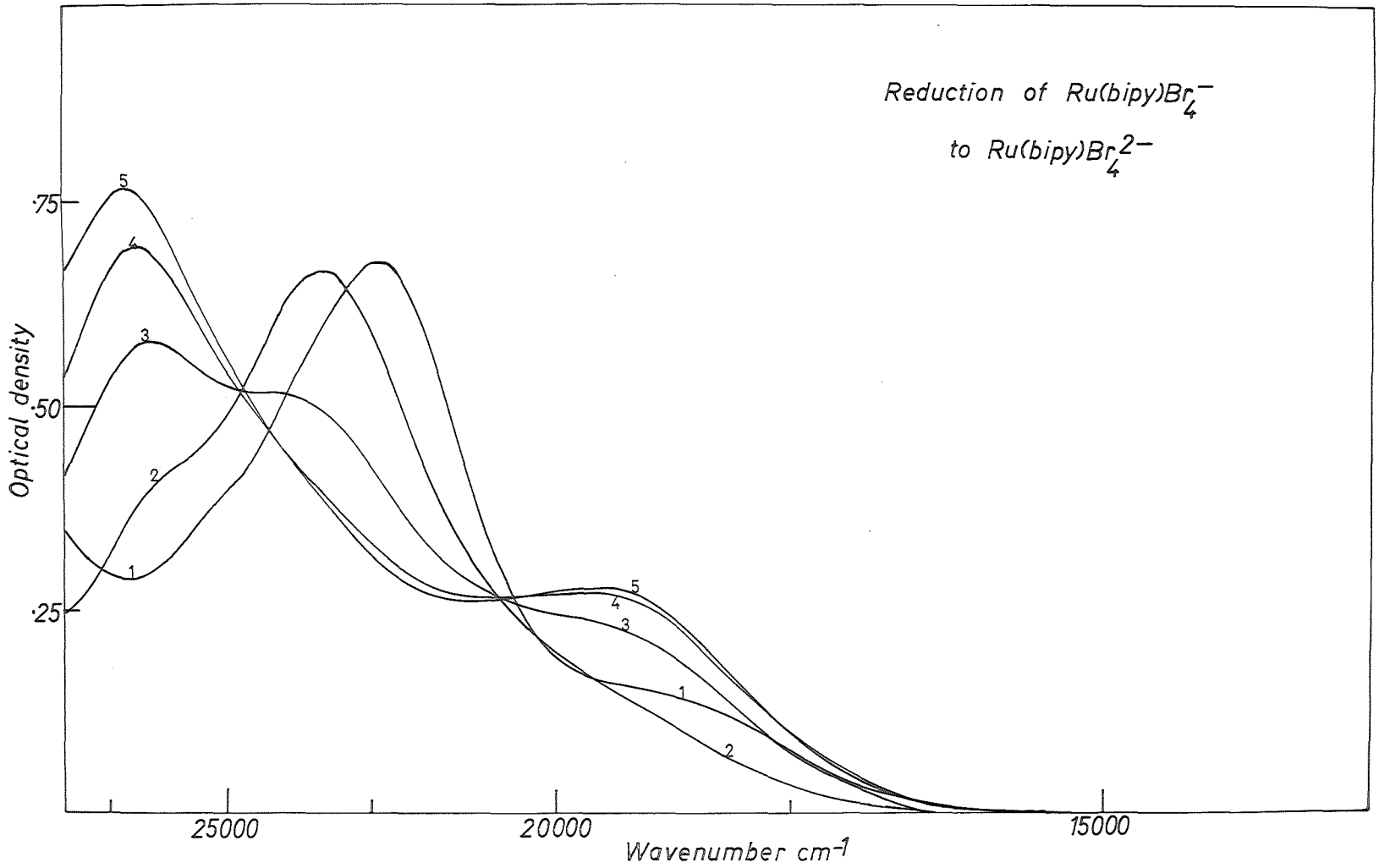

Optical density
·75
·50
·25
25000
20000
15000
Wavenumber cm⁻¹
Fe(bipy)(CN)₄²⁻ (MeOH)
Fe(bipy)₂(CN)₂ (MeOH)
Fe(bipy)₂(CN)₂ (CH₂Cl₂)

FIGURE 12


Reduction of Ru(bipy)Br4−
to Ru(bipy)Br4 2−
Optical density
·75
·50
·25
5
4
3
2
1
25000
20000
15000
Wavenumber cm-1

for the complex $(Ru(bipy)_2(CN)_2)$ (see page 83).

The trends in the energy of the band would indicate that the band is, like the lower energy band, associated with metal to ligand charge transfer, as ligand to metal charge transfer would show the reverse trends. (see Chapter IV) The energy of the band is also less than that expected for the lowest ligand to metal transition, $\pi \rightarrow e_g^*$ (to a first approximation, energy of $\pi \rightarrow \pi^*(1)$-energy of $t_{2g} \rightarrow \pi^*(1) + \Delta$).

Konig[4] has assigned the band at 29,000cm^{-1} in $(Fe(bipy)_2C_2O_4)$ to a transition associated with the bipyridyl ligand. This is unreasonable, since there is no sign of the transition in bipyridyl itself, and yet it is quite intense ($\varepsilon \simeq 10^4$) in the complexes. Also, the shifts in the band in all the complexes are much greater than those observed in the lower energy $\pi \rightarrow \pi^*(1)$ transition of the bipyridyl ligand.

Hanazaki and Nagakura[58] have assigned the band in the iron cation $(Fe(bipy)_3)^{2+}$ to three overlapping transitions from the metal t_{2g} to the second vacant π-antibonding orbital set in the bipyridyl. This explains the large bandwidth and is also consistent with the data obtained in the present work.

In the course of the present study, it was observed

that the separation between this higher energy band $t_{2g} \rightarrow \pi^*(2)$ and the $t_{2g} \rightarrow \pi^*(1)$ band at lower energy is similar in all the ruthenium complexes (~7500cm^{-1}). This is also the case in the iron complexes, although there the separation is about 9000cm^{-1}. The separation is also of the same order as that between the two intraligand transitions of the bipyridyl (~6700cm^{-1}).

However, there are several anomolies observed which would suggest a different assignment of this higher energy band. The mono-bipyridyl complexes show bands at similar energies to those in the bis-bipyridyl complexes. Whereas the intensity of the lower energy $t_{2g} \rightarrow \pi^*(1)$ band shows a marked decrease in intensity from a bis-bipyridyl to a mono-bipyridyl complex as expected, this band at higher energies shows a considerable increase in its intensity. (see Figs.10-12) This suggests that the number of ligands other than bipyridyl present determines the intensity of the transition, and that the correct assignment is a metal to other ligand X or Y (not bipyridyl) band.

This is not unreasonable in the case of pyridine complexes. Ford et al[83] in a study of a series of substituted pyridine complexes of the type $\left(Ru(NH_3)_5(py\text{-}X)\right)^{2+}$ found a strong band at ~24,000cm^{-1} which they assigned to a metal to pyridine charge transfer band. The presence of

bipyridyl in a pyridine containing complex cation e.g. $(Ru(bipy)_2(py)_2)^{2+}$, would tend to increase the energy of the band owing to increased metal to ligand π-bonding.

However, complexes which contain no bipyridyl but contain other ligands X and Y e.g. $(M(CN)_6)^{4-}$, $(M(en)_3)^{2+}$, $(M(H_2O)_2)^{2+}$ do not show the charge transfer transitions at ~27,000 cm^{-1} [3] found in bipyridyl complexes containing such ligands, indicating the transition is one associated with the bipyridyl. The relatively small change in the band position on changing the coordinated ligands, X and Y, compared with that expected for a metal to "other ligand" transition, and the presence of the band in complexes containing ligands which would not have suitable acceptor orbitals, as well as the presence of the band in the tris-bipyridyl complex $(Fe(bipy)_3)^{2+}$ all make the assignment of the transition to a metal to "other ligand" i.e. to X and Y, transition unlikely. However it does seem that the ligands other than bipyridyl do have a marked effect on the intensity of the band, but the reason for this is not known. In the pyridine complexes it could be due to the presence of a metal to pyridine band, superimposed on a metal to bipyridine band system, but it must be noted that other transitions involving the pyridine such as the $\pi \rightarrow \pi^*$ intraligand transitions are not observed in the bipyridyl/pyridine

complexes (see page 73) and the metal to pyridine charge transfer band may also be absent for similar reasons.

The Effects of Solvent

Schilt,[5] in a study of the effect of acid concentration on the spectra of the cyano complexes of iron, $(Fe(bipy)_2(CN)_2)$ and $K_2(Fe(bipy)(CN)_4)$ concluded that the cyanide ligands were protonated in strong acid solutions. Protonation will cause an increase in the metal to ligand π-bonding and thereby increase the energy of the $t_{2g} \rightarrow \pi^*$ transitions as was observed.

Polar solvents would also be expected to increase the energy of the transitions for a similar reason, and an increase in band energy is observed in the complex $(Fe(bipy)_2(CN)_2)$ on changing the solvent from dichloromethane to methanol, and in the complex $K_2(Fe(bipy)(CN)_4)$ on changing the solvent from methanol to water.

The spectrum of the ruthenium complex $(Ru(bipy)_2(CN)_2)$ in dimethylsulphoxide, a solvent of low polarity, is interesting. In methanol, only the low energy $t_{2g} \rightarrow \pi^*(1)$ transition at 21,740cm^{-1} is resolved. In dimethylsulphoxide this band is shifted to lower energy (19,960cm^{-1}) as expected. However, there is also another band at 28,900cm^{-1}, which corresponds to the higher energy $t_{2g} \rightarrow \pi^*(2)$ transitions.

It seems that in dimethylsulphoxide, the ligand field strength of the cyanide is decreased to the extent that this band, which is not resolved in methanol solution, is shifted to an energy sufficiently low for it not to be concealed by the $\pi \rightarrow \pi^*$ transition. This also indicates that the absence of the $t_{2g} \rightarrow \pi^*(2)$ band in $(Ru(bipy)_3)^{2+}$ and $(Ru(bipy)_2(NO_2)_2)$ is probably a result of it being hidden by the $\pi \rightarrow \pi^*(1)$ transition.

The tris-bipyridyl complexes are much less sensitive to changes in solvents, shifts in band energies being only $\sim 100 cm^{-1}$. Several other complexes e.g. the halogeno-complexes, $(M(bipy)_2X_2)$ and the pyridine complex cations $(M(bipy)_2(py)_2)^{2+}$ are also insensitive to changes in solvent. This indicates that the solvent effect is associated with the other coordinated ligands X and Y, rather than the bipyridyl.

The oxalato-complexes $(M(bipy)_2C_2O_4)$ and to a lesser extent the acetylacetonato-complexes $(M(bipy)_2acac)^+$ show solvent effects similar to those observed in the cyanide complexes i.e. the charge transfer bands shift to higher energy as the polarity of the solvent increases. (see Table 6). In the case of the oxalato-complex, it is probably the uncoordinated oxygen atoms which are interacting with the solvent.

The lower energy $\pi \rightarrow \pi^*(1)$ transition shows the same solvent effects as the charge transfer bands in the visible, though the energy shifts are, in general, much smaller.

Ligand Field Bands

Some authors e.g. Crosby[84] have assigned shoulders and weak bands at low energies in the divalent tris-bipyridyl complexes to ligand field bands. Palmer and Piper[76] have discussed these assignments. They estimated the ligand field parameters for these complexes, and concluded that the ligand field bands would be at least at the energies of the visible charge transfer spectra. They could not assign any bands to ligand field spectra for the cations $(Fe(bipy)_3)^{2+}$ and $(Ru(bipy)_3)^{2+}$ in polarized light studies of single crystals at low temperatures. The bands are concealed by the charge transfer spectra, and no assignments can be made.

FIGURE 13

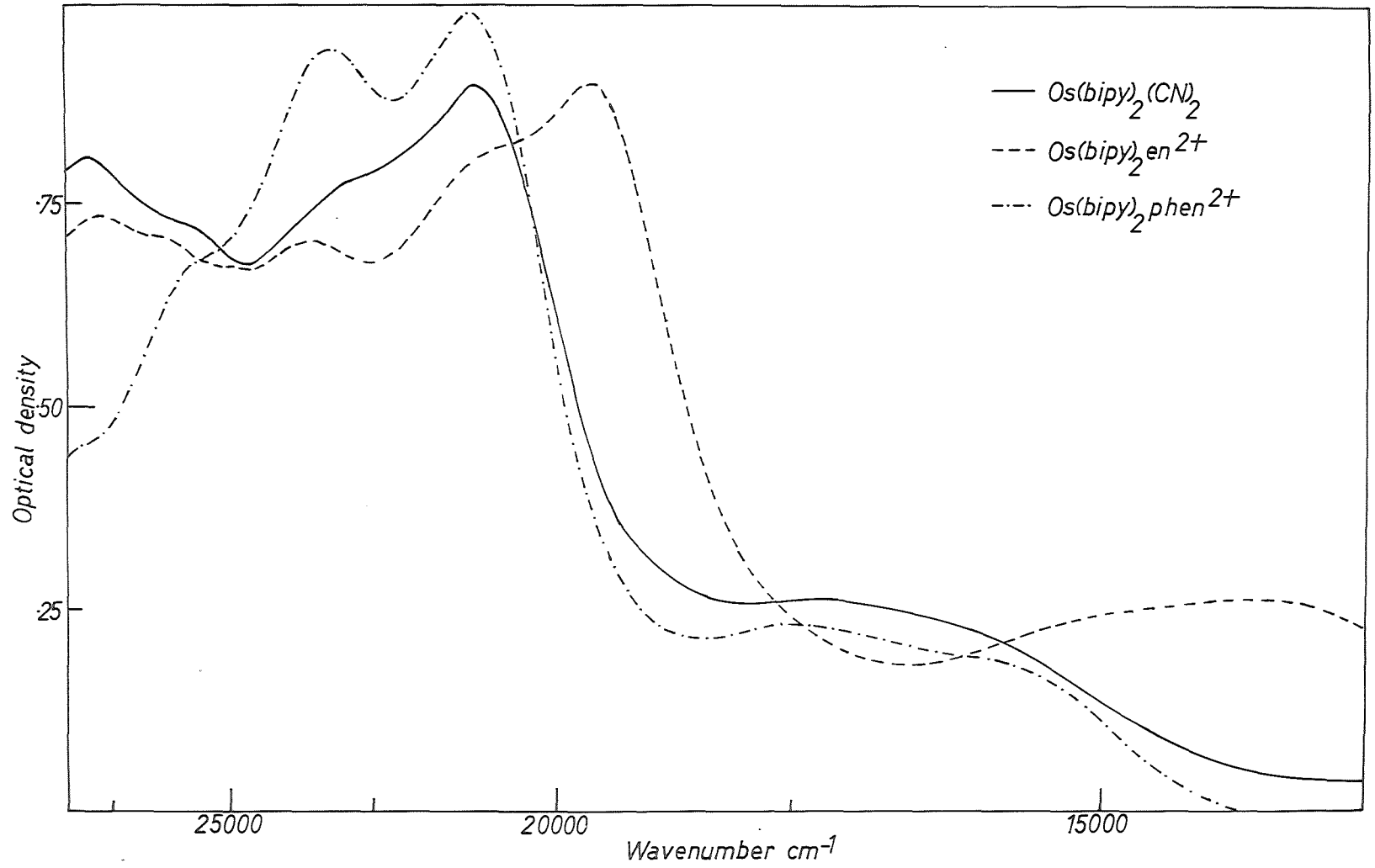

Os(bipy)2(CN)2
Os(bipy)2en2+
Os(bipy)2phen2+
·75
·50
·25
Optical density
25000
20000
15000
Wavenumber cm-1

FIGURE 14

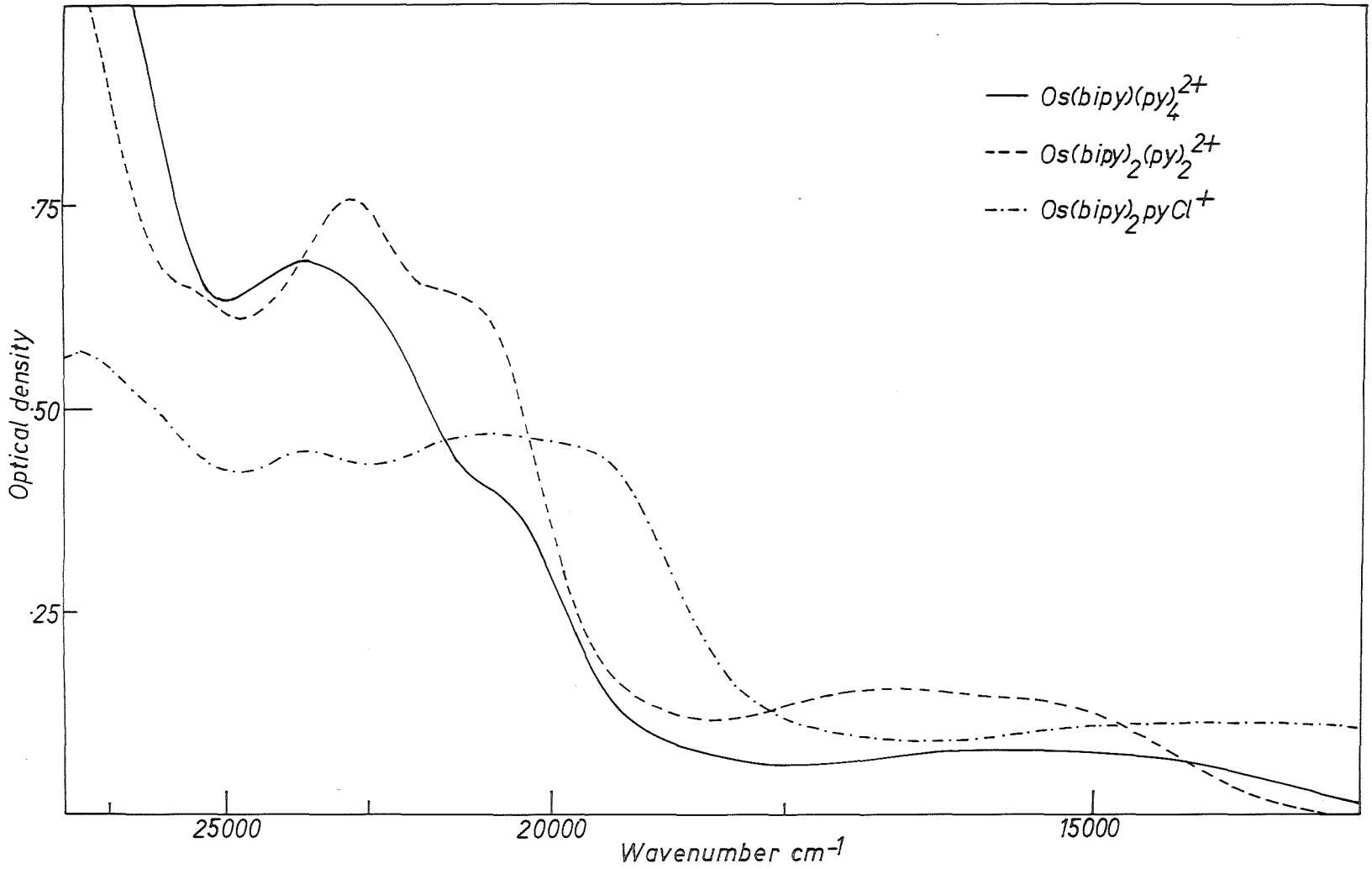
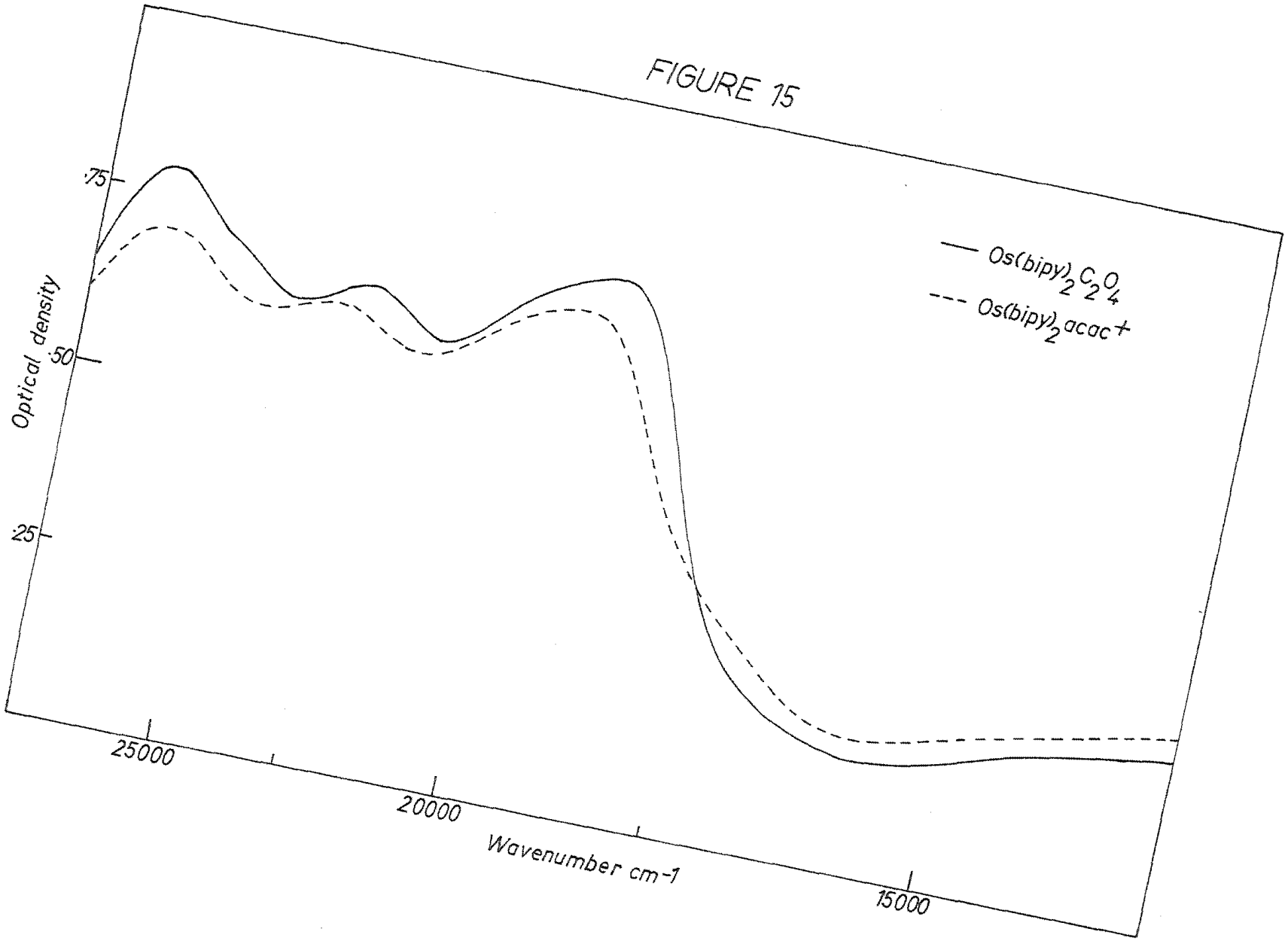

Os(bipy)(py)4 2+
Os(bipy)2(py)2 2+
Os(bipy)2pyCl+
·75
·50
·25
Optical density
25000
20000
15000
Wavenumber cm-1

FIGURE 15


Optical density
·75
·50
·25
25000
20000
15000
Wavenumber cm-1
Os(bipy)2C2O4
Os(bipy)2acac+

Visible Spectra of the Divalent Osmium Complexes

Numerical data for the spectra of the divalent osmium complexes are given in Table 4. Diagrams of typical spectra are given in Figs.13-15.

The visible spectra of the divalent osmium complexes show a much more complex system of bands than those observed in the corresponding iron and ruthenium compounds. The general appearance of the spectra seems to suggest a number of overlapping bands, and the pattern changes considerably when the coordinated ligands X and Y other than bipyridyl are changed.

All the complexes have a band of relatively low intensity ($\varepsilon \approx 3\times10^{3}$) at energies below 17,400cm^{-1}. In almost all cases the band is broad, and has a prominent shoulder to lower energies. The intensity of the band, particularly in the series of complexes containing pyridine, increases as the number of coordinated bipyridyl ligands increases. The band position shifts to higher energies as the ligand field strength of the coordinated ligands X and Y increases, and is at lower energies in the complex cation containing 4,4'-dimethylbipyridyl $(Os(4,4'\text{-diMebipy})_3)^{2+}$ than in the analogous bipyridyl cation, $(Os(bipy)_3)^{2+}$.

The tris complex cations $(Os(bipy)_3)^{2+}$ and $(Os(4,4'\text{-diMebipy})_3)^{2+}$, and other complexes containing strong field ligands e.g. $(Os(bipy)_2(CN)_2)$, and $(Os(bipy)_2phen)^{2+}$ show two main bands at higher energies, (~22,000cm^{-1} and ~27,000cm^{-1}) which are also split, in some cases into two peaks, and in others to a peak with a prominent shoulder. The relative intensities of the bands are difficult to determine, as the bands overlap to a considerable extent. The energy trends in these bands are similar to those found in the lower energy band at ~17,000cm^{-1}.

The complexes containing coordinated pyridine have a doublet at ~22,000cm^{-1}, but have a single band at ~28,000cm^{-1}. This band increases in intensity as the number of pyridine ligands coordinated increases. This is similar to the behaviour of the high energy metal-oxidation band in the corresponding ruthenium complexes (see page 81).

The complexes containing oxalate, $(Os(bipy)_2C_2O_4)$, acetylacetone $(Os(bipy)_2acac)^+$ and chloride $(Os(bipy)_2Cl_2)$ all show three well resolved bands with few shoulders. These also shift to higher energies as the ligand field strength of the coordinated ligands X and Y increases.

The ligand field bands in these osmium complexes would be expected to be at energies equal or greater than those of the corresponding ruthenium complexes. (see page 85)

The intensities of the major bands in the osmium complexes are too large for these to be assigned as ligand field bands although some of the shoulders could be associated with these. However no definite assignments can be made.

The band energies all show similar shifts as the coordinated ligands are changed. These are of the same order and are in the same direction as those in the $t_{2g} \rightarrow \pi^*$ transitions of the corresponding iron and ruthenium complexes already discussed. The assignment of the bands in the osmium complexes to metal oxidation transitions is therefore not unreasonable.

As already discussed on page 66, the ultraviolet spectra of the osmium complexes are very similar to those of the corresponding iron and ruthenium complexes. It seems likely then that it is the metal ion which is causing the marked differences in the visible spectra.

Spin orbit coupling (see Chapter II) is one effect which could cause splitting of the bands particularly in the osmium complexes, (although the spin orbit coupling constant is already quite large in ruthenium, and it is perhaps surprising that the spectra of the iron and ruthenium complexes are very similar). Spin selection rules will also be less important in the osmium complexes, and some of the weaker bands could perhaps be spin-forbidden transitions.

Other effects such as the lower symmetry of the complexes would be very similar in the iron and ruthenium complexes, and would not explain the changes in the visible spectrum of the osmium complexes.

Unfortunately it is not yet possible to determine which factors influence the spectra most, and it seems likely that several effects combine to give rise to the complex system of overlapping bands observed in the osmium compounds.

TABLE 2

SPECTRA OF THE BIPYRIDYL COMPLEXES OF IRON (II)

	(a)	$\pi\rightarrow\pi^*(2)$		$\pi\rightarrow\pi^*(1)$	$t_{2g}\rightarrow\pi^*(2)$		$t_{2g}\rightarrow\pi^*(1)$
$(Fe(bipy)_3)^{2+}$	ν	40570	(34600)	33560	28610	(20500)	19160
MeOH	ε	36200		60000	6280		8740
	δ			720			980
$(Fe(bipy)_2(CN)_2)$	ν	40570	(34530)	33370	27320	(19880)	18050
MeOH	ε	20900		46800	6170		6320
	δ			470	2690		1040
$(Fe(bipy)_2(CN)_2)$	ν	40320	(34070)	33160	25840		16470
CH_2Cl_2	ε	26400		55400	10060		10000
	δ			440	2210		760
$(Fe(bipy)(CN)_4)^{2-}$	ν		(34530)	33600	26670		18380
MeOH	ε			35900	5360		3870
	δ			260	2700		1660
$(Fe(bipy)(CN)_4)^{2-}$	ν		(33860)	33930	28990		20450
H_2O	ε			37900	4710		3910
	δ			460	3510		1470

Values in parenthesis indicate shoulders.

(a) ν = band energy in cm^{-1}, ε = extinction coefficient in $Moles^{-1}cm^{-1}$, δ = half-band-width in cm^{-1}.

TABLE 3

SPECTRA OF THE BIPYRIDYL COMPLEXES OF RUTHENIUM (II)

	(a)	$\pi\rightarrow\pi^*(2)$			$\pi\rightarrow\pi^*(1)$	$t_{2g}\rightarrow\pi^*(2)$		$t_{2g}\rightarrow\pi^*(1)$
$(Ru(bipy)_3)^{2+}$	ν	40930	(39420)		34980	(28740)	(23970)[b]	22080
MeOH	ε	25600			79200		6730	13700
	δ				1270		880	1140
$(Ru(bipy)_2(NO_2)_2)$	ν	~41700	(39500)		34770	(30300)		22850
MeOH	ε	21600			49800			7470
	δ				1250			1890
$(Ru(bipy)_2(CN)_2)$	ν	41120	(39450)		34710	(31250)		21740
MeOH	ε	17550			49600			7730
	δ				950			1330
$(Ru(bipy)_2(CN)_2)$	ν				33770	28900		19960
DMSO								
$(Ru(bipy)_2(py)_2)^{2+}$	ν	40980	(39370)	(36100)[b]	34530	29870	(23920)[b]	21740
MeOH	ε	23850		17500	50200	11100	4520	7840
	δ			740	1060	2520	1000	1330

(Cont.)

TABLE 3. (Continued)

$(Ru(bipy)(py)_4)^{2+}$	ν	40860	(39220)	(36100)[b]	34220		29000	(23580)[b]	21600	
MeOH	ε	26600		11270	35400		16200	2080	5720	
	δ	1450		1010	1080		2620	1000	1340	
$(Ru(bipy)_2pyCl)^{+}$	ν	40980		(35000)	34120	(32070)	28770		21370	(15500)
MeOH	ε	23650			43700		7140		4625	
	δ						3800		2190	
$(Ru(bipy)(py)_2I_2)$	ν	(42400)			33950		27250		20830	14620
MeOH	ε				26400		9220		3540	1022
	δ						2310		2450	1830
$(Ru(bipy)(py)_2Br_2)$	ν	40960		(34800)	33860		27780	(22720)[b]	20120	14750
MeOH	ε	18900			29500		8840	1460	4260	4000
	δ				810		2820	2150	1630	790
$(Ru(bipy)(py)_2Cl_2)$	ν	40820	(39840)	(34970)[b]	33720		27640	(21740)[b]	19930	
MeOH	ε	17100		14250	24700		1303	1930	4070	
	δ			620	680		2305	910	1130	
$(Ru(bipy)_2en)^{2+}$	ν	41000	(39200)	(35100)	34260		28700		20370	(17400)
MeOH	ε	21350			58100		7890		1000	
	δ				760		2600		1120	
$(Ru(bipy)_2(NH_3)_2)^{2+}$	ν	40980	(39220)	(34930)	34250	(31930)	28550		20220	(17100)
	ε	21800			58800		8020		9340	
	δ				750		2640		1120	

TABLE 3. (Continued)

$(Ru(bipy)_2acac)^+$	ν	40700	(36230)	(34970)	34010	27250		19700	(15340)
MeOH	ε	25900			50900	10530		8640	
	δ				660				
$(Ru(bipy)_2acac)^+$	ν	40350	(36050)	(34700)	33830	26880	(21980)[b]	19270	(17150)[b]
CH_2Cl_2	ε	28600			54250	11630	4350	9540	3830
	δ				680	2130	1340	1330	800
$(Ru(bipy)_2C_2O_4)$	ν	40820		(34970)	34090	27550		19380	(16250)
MeOH	ε	21050			54200	9050		8740	
	δ				670	2800		1430	
$(Ru(bipy)_2C_2O_4)$	ν	40820		(34250)	33560	26040		17830	
CH_2Cl_2	ε	26500			67400	13660		12570	
	δ				610	2510		2330	
$(Ru(bipy)_2(SCN)_2)$	ν	40700	(38900)	(34560)	33670	27590	(22800)	19360	(16100)
CH_2Cl_2	ε	30150			49300	8760		8200	
	δ				650	2600		1440	
$(Ru(bipy)_2I_2)$	ν	40650		(34250)	33410	26250		18400	(15100)
CH_2Cl_2	ε	35200			39900	9210		8340	
	δ				730	2350			
$(Ru(bipy)_2Br_2)$	ν	40820		(34620)	33440	26810	(20580)[b]	18360	(15870)
CH_2Cl_2	ε	33200			52500	10160	4700	9710	~2100
					560	2800	1030	1085	

TABLE 3. (Continued)

$(Ru(bipy)(acac)_2)$ [c]	ν	(40650)	(38910)	35900	(33670)	24040	16100
CH_2Cl_2	ε			26200		9400	4980
						3100	1240
$(Ru(bipy)Cl_4)^{2-}$ [d]	ν					27250	19690
(H_2O)							
$(Ru(bipy)Br_4)^{2-}$ [d]	ν					27400	19920
(H_2O)							

Values in parenthesis indicate shoulders.

(a) ν = band energy in cm^{-1}, ε = extinction coefficient in $Moles^{-1}$ cm^{-1}, δ = half-band-width in cm^{-1}.

(b) Resolved into Gaussian components (see page 131)

(c) May be some decomposition in solution.

(d) Prepared only in solution (see page 20).

TABLE 4

SPECTRA OF THE BIPYRIDYL COMPLEXES OF OSMIUM (II)

Compound and Solvent	(a)	π→π*(2)			π→π*(1)								
$(Os(bipy)_3)^{2+}$	ν	41010	(39340)		34500		27210	(25970)		22940	(22370)	20920	17270	(15620)
MeOH	ε	27400			77300		9550	9020		10660		11100	3270	
	δ				1080									
$(Os(4,4'\text{-diMebipy})_3)^{2+}$	ν	40290	(38820)		34480	29970	26700	(25510)		(22370)	21740	20350	16780	(15460)
MeOH	ε	27200			88700	11600	12400				13400	13500	3880	
	δ				960									
$(Os(bipy)_2phen)^{2+}$	ν		(39060)	37510[b]	34500		(28130)	(25550)		23200		20990	17390	15820
MeOH	ε			55100	64500					14400		14800	4160	
	δ				1070									
$(Os(bipy)_2(CN)_2)$	ν	41180			34400	(30330)	27970	(25810)		(22780)		21050	17280	
MeOH	ε	20900			59700	7810	7790					8790	2540	
	δ				840									
$(Os(bipy)_2en)^{2+}$	ν	40820			33940		27860	(26320)	23530	(20840)		19590	(14930)	13930
MeOH	ε				56500		8250		7960			10150		3040
	δ				830									
$(Os(bipy)(en)_2)^{2+}$	ν	(41670)			34620					23150		(20790)	(17240)	
MeOH	ε				25800					10000				
	δ				1550									

(Cont.)

TABLE 4. (Continued)

$(Os(bipy)_2(py)_2)^{2+}$	ν	(41320)		34120	28760		(25580)	22780		(21190)	16470 (15220)
MeOH	ε			58600	15700			11500			2460
$(Os(bipy)(py)_4)^{2+}$	ν	40740		33710	28090		(23550)	20680			15750 (14790)
MeOH	ε	27100		30900	19040		11900	6940			1390
	δ			1010							
$(Os(bipy)_2pyCl)^{+}$	ν	(40820)		33830	28170		23530	20750		(19460)	14270
MeOH	ε			33400	7450		5910	6220			1560
	δ			810							
$(Os(bipy)_2pyBr)^{+}$	ν	(40980)		33780	28090		23530	20920		(19530)	14290 (13510)
MeOH	ε			31400	7360		5380	5670			1340
	δ			820							
$(Os(bipy)_2acac)^{+}$	ν	40940	(36360)	33850	26710		22850		19210		13350
MeOH	ε	28800		48100	10200		9470		10300		4010
	δ			960							
$(Os(bipy)_2C_2O_4)$	ν	40720		33920	26760	(24940)	22320		18820		13050
MeOH	ε	35200		79500	15500		13500		14950		5050
	δ			940							
$(Os(bipy)_2Cl_2)$ [c]	ν				26110		21480		17910		11880

(Cont.)

TABLE 4. (Continued)

Values in parenthesis indicate shoulders.

(a) ν = band energy in cm^{-1}, ε = extinction coefficient in $Moles^{-1}\ cm^{-1}$, δ = half-band-width in cm^{-1}.

(b) Intraligand transition of 1,10-phenanthroline.

(c) See also ref.7.

TABLE 5

ENERGIES OF THE PRINCIPAL INTRALIGAND BANDS FOR THE DIVALENT COMPLEXES

Compound	Solvent	Osmium		Ruthenium		Iron	
		$\pi\rightarrow\pi^*(1)$	$\pi\rightarrow\pi^*(2)$	$\pi\rightarrow\pi^*(1)$	$\pi\rightarrow\pi^*(2)$	$\pi\rightarrow\pi^*(1)$	$\pi\rightarrow\pi^*(2)$
$(M(bipy)_3)^{2+}$	MeOH	34500	41010	34980	40930	33400	40570
$(M(bipy)_2(CN)_2)$	MeOH	34400	41180	34710	41120	33370	40570
"	CH_2Cl_2					33080	40320
$(M(bipy)(CN)_4)^{2-}$	MeOH					33600	
$(M(bipy)_2(NO_2)_2)$	MeOH			34770	(41700)		
$(M(bipy)_2(py)_2)^{2+}$	MeOH	34120	(41320)	34530	40980		
$(M(bipy)(py)_4)^{2+}$	MeOH	33710	40740	34220	40860		
$(M(bipy)(py)_2Cl_2)$	MeOH			33720	40820		
$(M(bipy)_2pyCl)^{+}$	MeOH	33830	(40820)	34120	(40880)		
$(M(bipy)_2pyBr)^{+}$	MeOH	33780	(40980)				
$(M(bipy)_2en)^{2+}$	MeOH	33940	40820	34260	41000		
$(M(bipy)_2(NH_3)_2)^{2+}$	MeOH			34250	40980		
$(M(bipy)_2C_2O_4)$	MeOH	33920	40720	34090	40820	34700 [a]	41000 [a]
$(M(bipy)_2acac)^{+}$	MeOH	33850	40490	34010	40700		
"	CH_2Cl_2			33830	40350		
$(M(bipy)_2Cl_2)$ [b]	CH_2Cl_2	33400		33400		34200	40800
$(M(bipy)_2I_2)$ [b]	CH_2Cl_2	33500		33410			

Values in parenthesis indicate shoulders. Energy of the transitions in cm^{-1}. (a) See ref.4 (b) See ref.7.

TABLE 6

ENERGIES OF THE PRINCIPAL CHARGE TRANSFER BANDS FOR THE DIVALENT IRON AND RUTHENIUM COMPLEXES

Compound	Solvent	Ruthenium		Iron	
		$t_{2g}\rightarrow\pi^*(2)$	$t_{2g}\rightarrow\pi^*(1)$	$t_{2g}\rightarrow\pi^*(2)$	$t_{2g}\rightarrow\pi^*(1)$
$(M(bipy)_2(NO)_2)$	MeOH		22850		
$(M(bipy)_3)^{2+}$	MeOH		22080	28610	19160
$(M(bipy)_2(CN)_2)$	MeOH		21740	27320	18050
	CH_2Cl_2			25810	16470
	DMSO	28900	19960		
$(M(bipy)(CN)_4)^{2-}$	MeOH			26670	18380
	H_2O			28990	20450
$(M(bipy)_2(py)_2)^{2+}$	MeOH	29870	21740		
$(M(bipy)(py)_4)^{2+}$	MeOH	29000	21600		
$(M(bipy)_2pyCl)^{+}$	MeOH	28770	21370		
$(M(bipy)_2en)^{2+}$	MeOH	28700	20370		
$(M(bipy)_2(NH_3)_2)^{2+}$	MeOH	28550	20220		
$(M(bipy)(py)_2Br_2)$	MeOH	27780	20120		
$(M(bipy)(py)_2Cl_2)$	MeOH	27640	19930		
$(M(bipy)_2acac)^{+}$	MeOH	27250	19700		

(Cont.)

TABLE 6 (Continued)

$(M(bipy)_2C_2O_4)$	MeOH	27550	19380	29000[a]	19200[a]
	CH_2Cl_2	26040	17830		
$(M(bipy)_2(SCN)_2)$	CH_2Cl_2	27590	19360		
$(M(bipy)_2Br_2)$	CH_2Cl_2	26810	18360		
$(M(bipy)_2Cl_2)$[b]	CH_2Cl_2	26460	18020	27780	18870
$(M(bipy)Cl_4)^{2-}$	H_2O	27250	19690		
$(M(bipy)Br_4)^{2-}$	H_2O	27400	19920		

Energies in cm^{-1}.

(a) See ref.7 (b) See ref.4

TABLE 10

SPECTRA OF THE DIVALENT COMPLEXES OF 4,4'-DIMETHYLBIPYRIDYL

Compound and Solvent	(a)	$\pi\rightarrow\pi^*(2)$			$\pi\rightarrow\pi^*(1)$	$t_{2g}\rightarrow\pi^*(2)$		$t_{2g}\rightarrow\pi^*(1)$
$(Fe(4,4'\text{-diMebipy})_3)^{2+}$	ν	39840		(34800)	33740	28210	(20390)	18900
MeOH	ε	25200			66400	7660		9060
	δ				690			1000
$(Fe(4,4'\text{-diMebipy})_2(CN)_2)$	ν	39950		(34840)	33650	26880		18180
MeOH	ε	10400			21900	3850		2630
	δ				530	3200		1120
$(Fe(4,4'\text{-diMebipy})(CN)_4)^{2-}$	ν			(35290)	34190	29530		21280
H_2O	ε				23000	3200		2460
	δ				550	4190		1900
$(Ru(4,4'\text{-diMebipy})_3)^{2+}$ (b)	ν	41060	39060					21740
H_2O	ε	23500	21900		67000			9180
	δ							
$(Ru(4,4'\text{-diMebipy})_2acac)^{+}$	ν	40080	(38800)	(35000)	34110	26930		19460
MeOH	ε	23800			47100	9940		7360
	δ				710			

(Cont.)

TABLE 10 (Continued)

$(Ru(4,4'\text{-diMebipy})_2(NH_3)_2)^{2+}$	ν	40320	(38800)	(35640)	34340	28390	(22050)	20000
MeOH	ε	18900			60400	8420		9070
	δ				740	3000		1210
$(Ru(4,4'\text{-diMebipy})_2(CN)_2)$	ν	40410	(38900)		34790			22120
MeOH	ε	15300			45100			6620
	δ				990			1630
$(Os(4,4'\text{-diMebipy})_3)^{2+}$ (c)								

Values in parenthesis indicate shoulders.

(a) ν = band energy in cm^{-1}, ε = extinction coefficient in $Moles^{-1}\ cm^{-1}$, δ = half-band-width in cm^{-1}

(b) See ref.24.

(c) See Table 4.

CHAPTER IV

ELECTRONIC ABSORPTION SPECTRA OF COMPLEXES OF BIPYRIDYL WITH TRIVALENT IRON, RUTHENIUM AND OSMIUM

INTRODUCTION

The spectra of the complexes of bipyridyl with trivalent iron, ruthenium and osmium are somewhat more complex than those of the corresponding divalent compounds. The absorptions in the visible region have differing origins, depending on the type of ligands other than bipyridyl coordinated. The ultraviolet spectra also show marked changes on changing the metal ion and the coordinated ligands.

The compounds studied in the present work fall into three major groups, each with its own distinctive features, although there is some overlapping between the groups. These are:

1. The $(M(bipy)_3)^{3+}$ group, which consists of the tris bipyridyl complexes and bis- or mono-bipyridyl complexes containing ligands such as pyridine, 1,10-phenanthroline and the cyanide ion.

2. The bipyridyl halogeno-complexes, which are the bipyridyl complexes containing coordinated halogens.

3. The bipyridyl acetylacetonato-complexes, which contain coordinated acetylacetone.

The $(M(bipy)_3)^{3+}$ Group

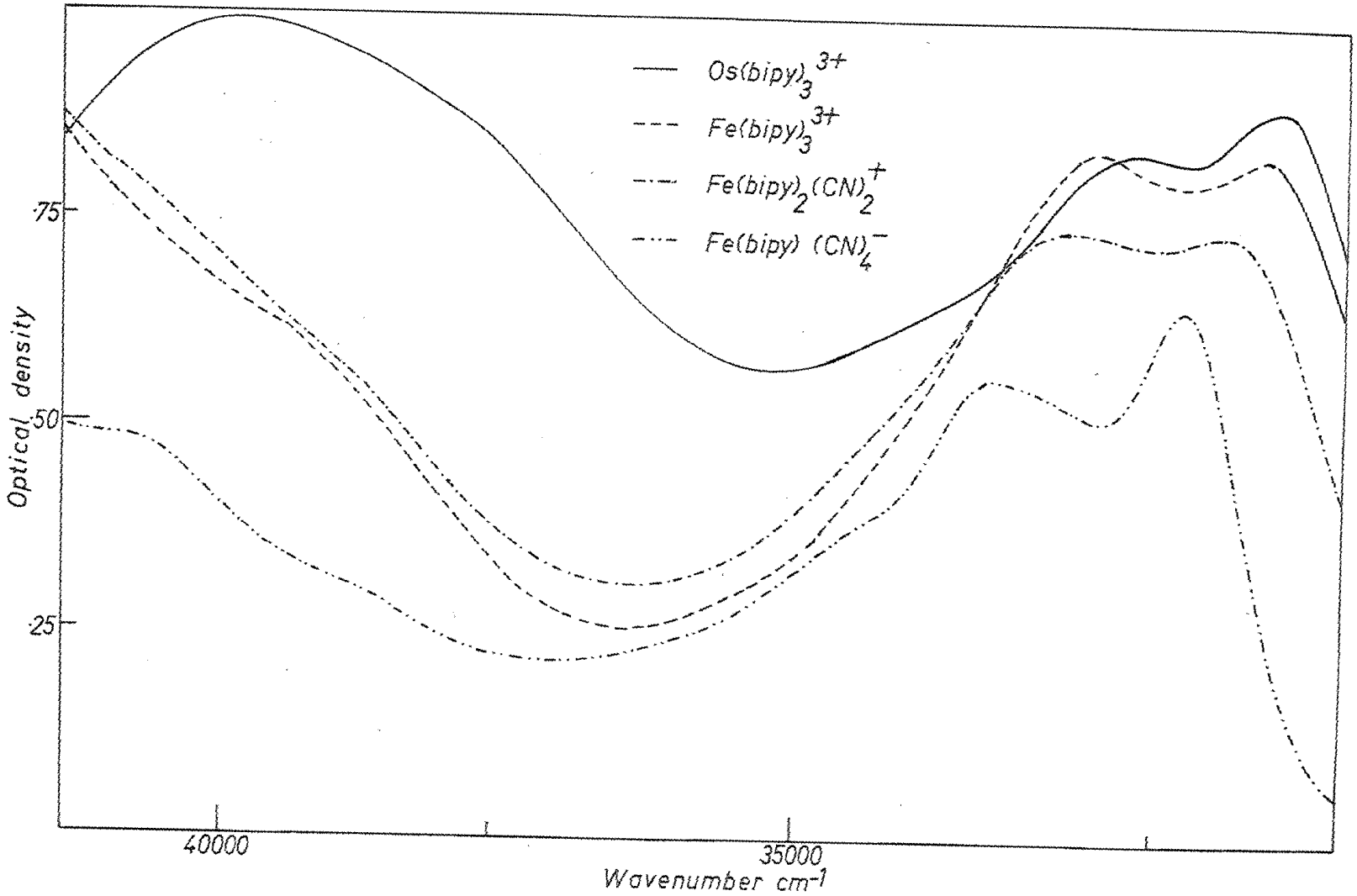
The numerical data for the spectra of the complexes in the $(M(bipy)_3)^{3+}$ group are given in Table 7. Diagrams of typical spectra are given in Figs.16-21.

The ultraviolet spectra of these complexes consist of a band at ~42,000cm^{-1} ($\varepsilon>10^4$) and another characteristic band which is resolved into two components at ~32,600cm^{-1} and ~31,600cm^{-1} ($\varepsilon>2\times10^4$) and in some cases also has several shoulders on the high energy side. Like the ultraviolet transitions in the divalent complexes (see page 66) these bands may be assigned to the intraligand transitions of bipyridyl.

The major feature of the visible spectra is a much weaker band ($\varepsilon<6\times10^2$) at energies below 19,000cm^{-1}. This has been assigned to a ligand to metal charge transfer transition. There are also a few other bands common to only one or two of the complexes.

The spectra of the trivalent tris-bipyridyl complexes have been studied much less than the corresponding divalent derivatives. Williams[75] and Weber[68] have studied the spectra of the tris-bipyridyl iron complex ion, $(Fe(bipy)_3)^{3+}$. Schilt[5] has reported the visible spectra of the bipyridyl complexes of iron containing coordinated cyanide, and Miller et al[27] have reported the visible spectra of two

FIGURE 21


Os(bipy)$_3^{3+}$
Fe(bipy)$_3^{3+}$
Fe(bipy)$_2$(CN)$_2^{+}$
Fe(bipy) (CN)$_4^{-}$
·75
·50
·25
Optical density
40000
35000
Wavenumber cm^{-1}

ruthenium derivatives. Recently Mason et al[70] have reported the circular dichroism and spectral measurements for the tris cations $(Ru(bipy)_3)^{3+}$ and $(Os(bipy)_3)^{3+}$, although the spectrum given for the ruthenium complex may be in error (see page 132).

Intraligand Transitions

Lower Energy $\pi \rightarrow \pi^*(1)$ Transition.

The lower energy transition in the ultraviolet spectra of the complexes of the $(M(bipy)_3)^{3+}$ group (see Table 7 and Fig.21) is assigned to an intraligand transition of bipyridyl for reasons similar to those used for the corresponding transition in the divalent complexes (see page 66). There is a marked decrease in intensity as the number of coordinated bipyridyls in the complex is reduced. The assignment of the band to a charge transfer band is unreasonable since a similar transition occurs in the trivalent tris-bipyridyl complexes of cobalt, rhodium and iridium.[79,80] Any charge transfer band would be expected to be at different energies for the iron group compared to the cobalt group.

The splitting of the band into two resolved peaks, separated by a nearly constant amount ($\sim 1100 cm^{-1}$) in all the complexes in marked contrast to the divalent complexes, where the splitting of the peaks is much less and varies considerably as the metal ion and

coordinated ligands X and Y are changed (see page 71). This constant value for the splitting suggests it may be largely due to a vibrational effect, but the reasons for the difference in the splitting of the band in the divalent and the trivalent complexes are not understood.

The energies of the band in the $(M(bipy)_3)^{3+}$ group change as the metal ion and coordinated ligands are changed, but the shifts are very much less than those observed in the corresponding divalent complexes. However, for a particular metal ion, the shifts are in the same direction as those in the divalent complexes, the band being at lower energies in complexes containing weak field ligands X and Y. For example, the bands are at higher energies in the tris-complex cation $(Os(bipy)_3)^{3+}$ than in the pyridine complex cation, $(Os(bipy)_2(py)_2)^{3+}$, pyridine having a smaller ligand field effect than bipyridyl.

For the iron series, there is a decrease in energy of the transition in the order $(Fe(bipy)(CN)_4)^-$ > $(Fe(bipy)_2(CN)_2)^+$ > $(Fe(bipy)_3)^{3+}$. (see Table 7 and Fig.21) Unfortunately, owing to experimental difficulties there is little data available for the ruthenium complexes (see page 132).

For the trivalent complexes of iron, ruthenium and osmium it is possible to determine the relative energy of the t_{2g} orbital from the observed energy of the $\pi \rightarrow t_{2g}$

transition. (see page 99). This shows that the t_{2g} level is at lower energy in the iron complex, $(Fe(bipy)_3)^{3+}$ than in the osmium complex, $(Os(bipy)_3)^{3+}$. The $\pi\rightarrow\pi^*(1)$ transition is at higher energy in the iron complex, as expected from the study of the divalent complexes (see page 69) where it has been found that the lower the energy of the t_{2g} level, the higher the energy of the $\pi\rightarrow\pi^*(1)$ transition. However, when all the complexes of the $(M(bipy)_3)^{3+}$ group are considered it is found that this relationship between the energy of the t_{2g} level and the energy of the $\pi\rightarrow\pi^*$ transition does not always hold. For example, the $\pi\rightarrow\pi^*(1)$ transition is at higher energy in the cyano-complex $(Fe(bipy)(CN)_4)^-$ than in the osmium complex $(Os(bipy)_3)^{3+}$, although the t_{2g} level is at higher energy in the cyano-complex.

The reasons for these effects are not understood, but they may be at least partly due to the higher charge on the trivalent metal ion. The trivalent complexes would also be expected to form stronger σ-bonds but weaker π-bonds than the corresponding divalent complexes.

Higher Energy $\pi\rightarrow\pi^*(2)$ Transition.

The second intraligand transition of bipyridyl occurs at 40,980cm^{-1}, and shifts to higher energies on protonation (see page 54). In the trivalent iron bipyridyl complexes

there is a strong absorption above 45,500cm^{-1} with several shoulders at ~40,000cm^{-1}. A strong broad band at ~40,000cm^{-1} occurs for the cations $(Ru(bipy)_2acac)^{2+}$, $(Os(bipy)_3)^{3+}$, $(Os(4,4'\text{-diMebipy})_3)^{3+}$ and $(Os(bipy)_2(py)_2)^{3+}$, with a shoulder at lower energy in the last three compounds. The spectrum of the cation $(Os(bipy)_2(phen))^{3+}$ is complicated by the presence of an intraligand transition in the 1,10-phenanthroline ligand, but it also has this intense band at ~40,000cm^{-1}. The high intensity of the band is unexpected as in almost all the other bipyridyl complexes studied the intensity of the high energy $\pi\rightarrow\pi^*(2)$ transition is less than or equal to that of the $\pi\rightarrow\pi^*(1)$ transition. There is a possibility that the band is the $\pi\rightarrow\pi^*(2)$ transition together with some other component, of charge transfer origin.

A metal reduction band of the type $\pi\rightarrow e_g^*$ would probably have energy of the right order, but the transition in the iron complexes would be expected to be at equal or lower energy than the ones in the osmium complexes. However the observed band is at much higher energies in the iron complexes. A metal oxidation band of the type $t_{2g}\rightarrow\pi^*$ is also unlikely because of the large difference in energy between the observed band in the iron and osmium complexes. The origin of the components of the band must therefore remain uncertain.

FIGURE 16

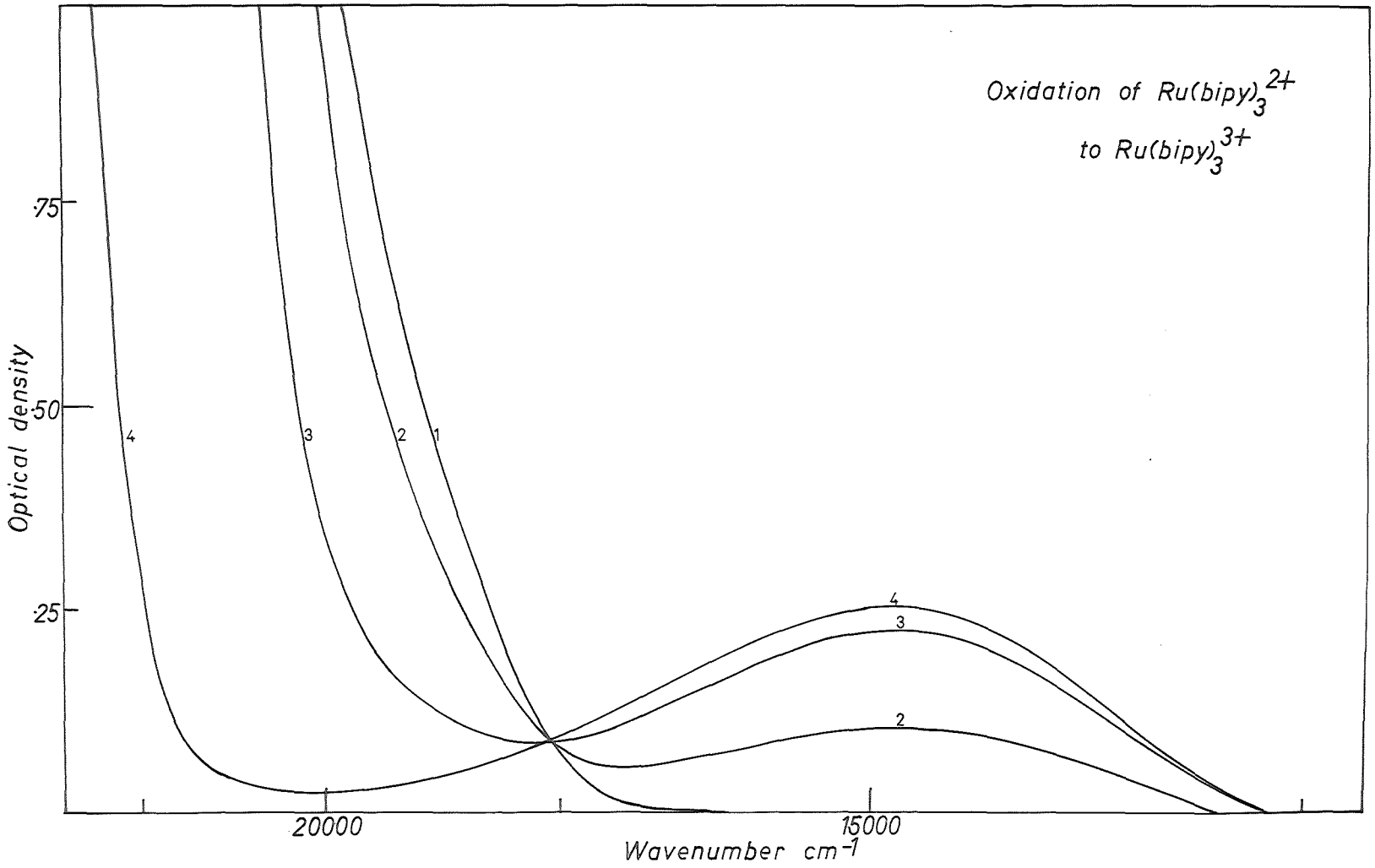

Oxidation of Ru(bipy)$_3^{2+}$
to Ru(bipy)$_3^{3+}$
.75
.50
.25
Optical density
4
3
2
1
4
3
2
20000
15000
Wavenumber cm^{-1}

FIGURE 17

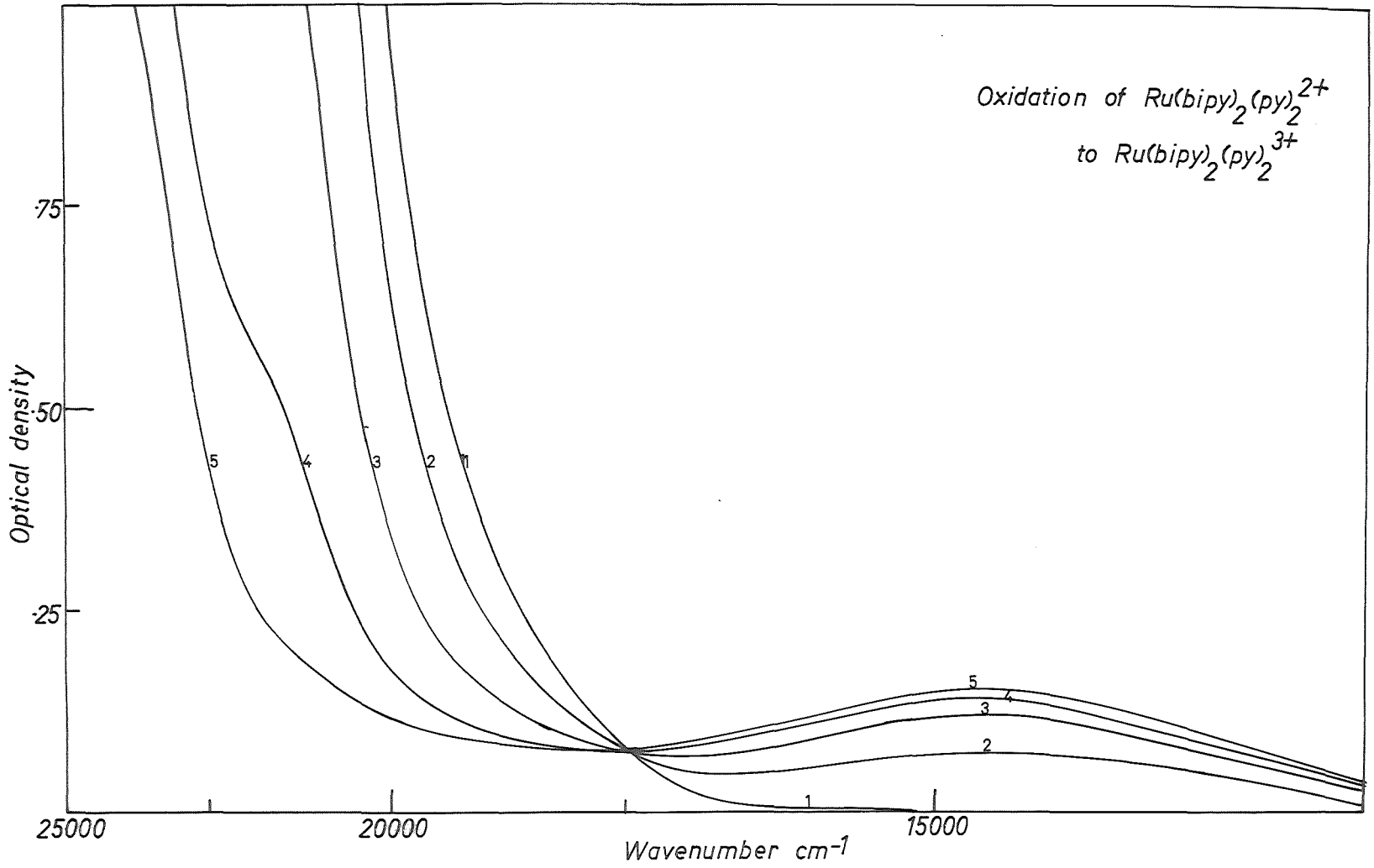

Oxidation of $Ru(bipy)_2(py)_2^{2+}$
to $Ru(bipy)_2(py)_2^{3+}$
Optical density
.75
.50
.25
5
4
3
2
1
25000
20000
15000
Wavenumber cm^{-1}

FIGURE 19

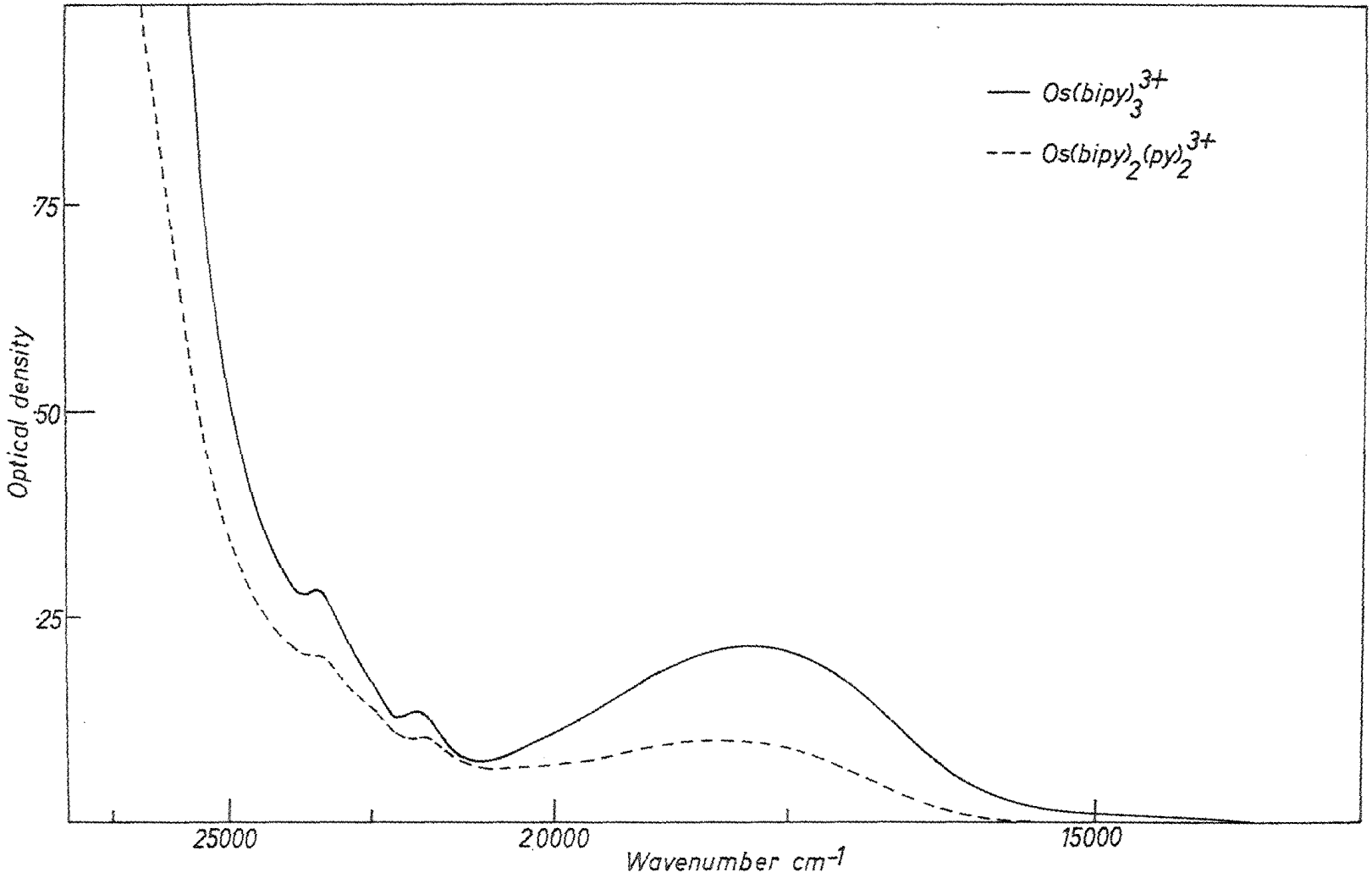

Os(bipy)$_3^{3+}$
Os(bipy)$_2$(py)$_2^{3+}$
Optical density
.75
.50
.25
25000
20000
15000
Wavenumber cm^{-1}

FIGURE 20

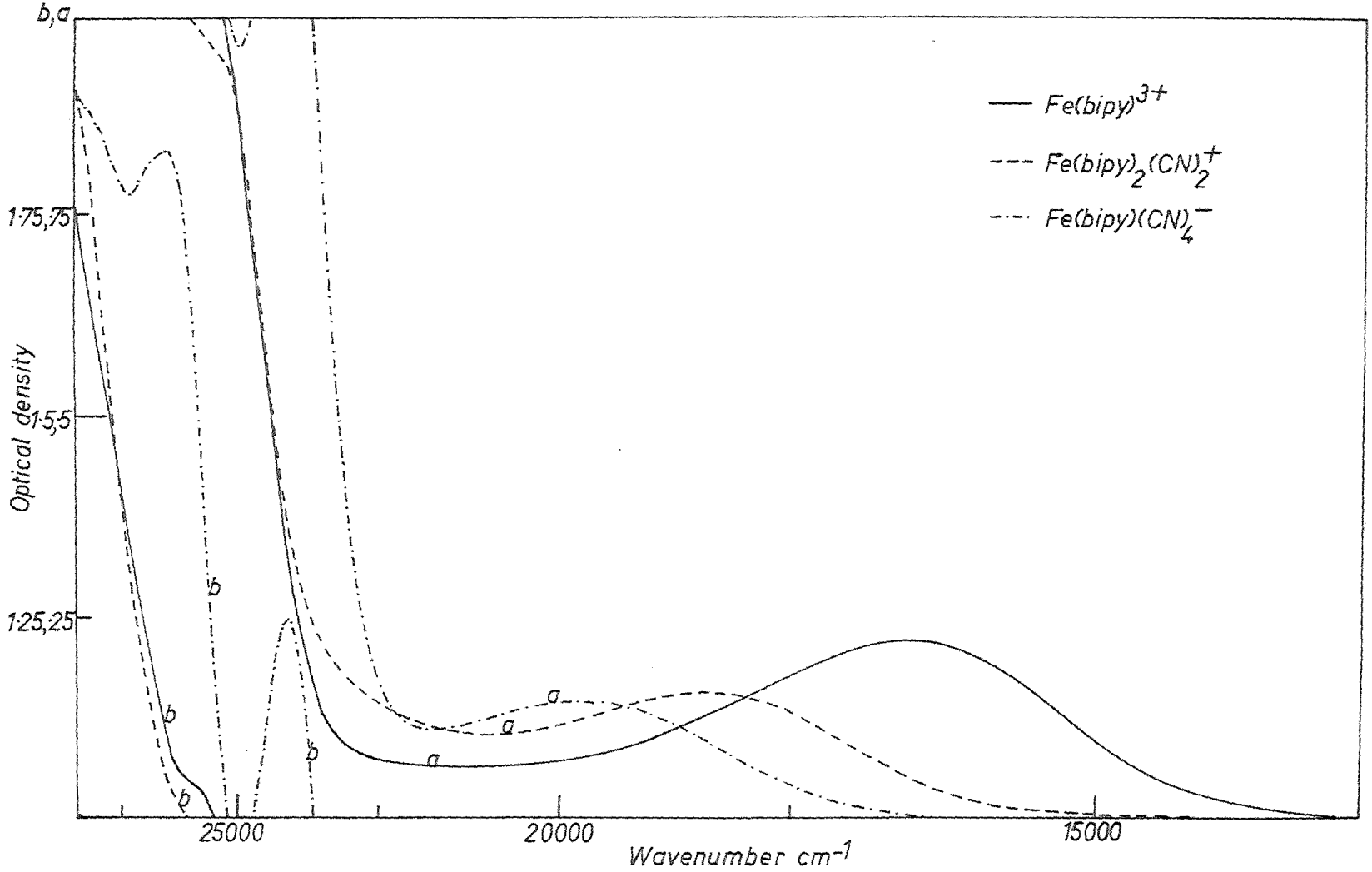
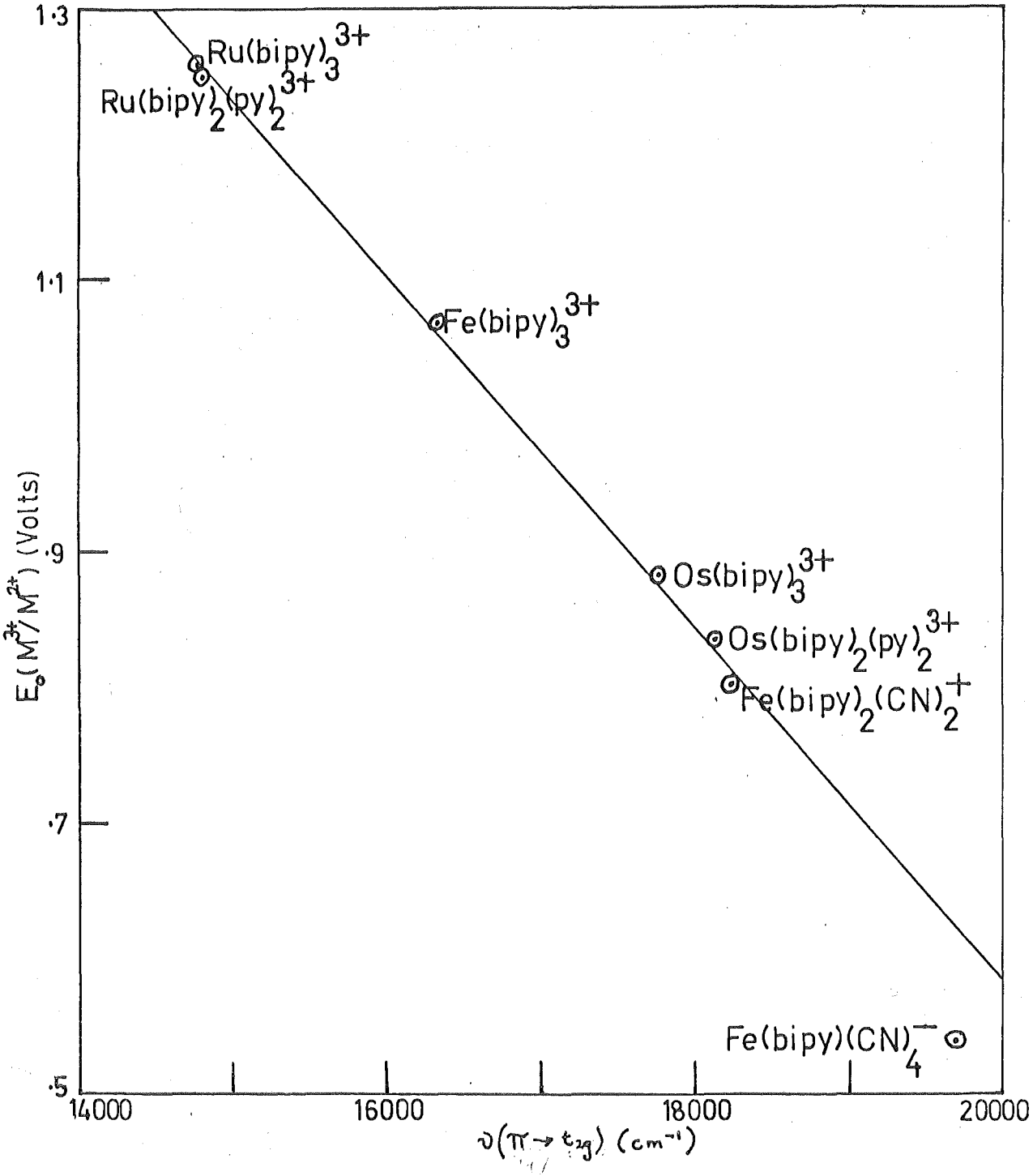

b,a
1·75,75
1·5,5
1·25,25
Optical density
25000
20000
15000
Wavenumber cm⁻¹
Fe(bipy)3+
Fe(bipy)2(CN)2+
Fe(bipy)(CN)4−

FIGURE 22


1·3
1·1
·9
·7
·5
$E_o(M^{3+}/M^{2+})$ (Volts)
$Ru(bipy)_3^{3+}$
$Ru(bipy)_2(py)_2^{3+}$
$Fe(bipy)_3^{3+}$
$Os(bipy)_3^{3+}$
$Os(bipy)_2(py)_2^{3+}$
$Fe(bipy)_2(CN)_2^{+}$
$Fe(bipy)(CN)_4^{-}$
14000
16000
18000
20000
$\bar{\nu}(\pi \rightarrow t_{2g})$ (cm^{-1})

Ligand to Metal Charge Transfer Band

All of the complexes of the $(M(bipy)_3)^{3+}$ group have a weaker band ($\varepsilon<6\times10^2$) at energies below 19,000cm^{-1} (see Table 7 and Figs.16-20).

The band intensity decreases as the number of coordinated bipyridyl ligands in the complexes decreases, indicating that the transition is associated with the bipyridyl ligand. The effects of substituents in the coordinated bipyridyl on the spectra of the trivalent tris-bipyridyl iron complexes have been studied by Williams.[75]

The observed shifts in the energy of the band were found to be smaller and in the opposite direction to those found for the visible transitions of the divalent complexes, where the bands have been assigned to a metal-oxidation $t_{2g}\rightarrow\pi^*$ transition (see page 96). These shifts are consistent with the assignment of the transition to a ligand to metal charge transfer transition. A similar assignment has been made by Mason[70] and, for the iron tris-1,10-phenanthroline complexes, by Day and Sanders.[59]

Further evidence that the band is associated with a metal reduction process is given by the observed linearity of a plot of transition energy against the oxidation potential of the corresponding divalent-trivalent couples (see Fig.22). The oxidation potentials have been measured by Buckingham,[91] Goodgame[85] and George et al.[86] The most

negative oxidation potentials correspond to the lowest energy transitions, as expected for a trivalent metal reduction process. This observed linearity is perhaps surprising, since the oxidation potential of a complex will be influenced by many factors e.g. solvation energies, other than electronic effects. However, with the exception of the iron bipyridyl cyano-complexes, the complexes will all have the same charge and will be of approximately the same molecular size. Therefore such effects as solvation energies may well be reasonably constant for the series.[91]

The transition has been assigned to a ligand to metal charge transfer. The ligand orbital involved will be one of the filled π-molecular orbitals of the bipyridyl, and the vacant metal orbital will be of t_{2g} type. The metal orbital is unlikely to be one of the e_g^* orbitals for a $\pi \rightarrow e_g^*$ transition would be expected at much higher energy, and the energy of the transition in the ruthenium cation $(Ru(bipy)_3)^{3+}$ ($14{,}790 cm^{-1}$) is even less than the expected ligand field splitting for this complex. There is also no strong transition at lower energies which could be assigned to a $\pi \rightarrow t_{2g}$ band.

The intensity of the band is low for an allowed charge transfer band, and this may suggest that it is associated with a ligand field band. However, Gray[61] has assigned the ligand field bands in ferricyanide, $(Fe(CN)_6)^3$, and

osmicyanide, $(Os(CN)_6)^{3-}$, and calculates a value for Δ of 34,950cm^{-1} for ferricyanide. Although bipyridyl would not be expected to produce a ligand field splitting as great as that of the cyanide ion, assignment of a transition at 14,790cm^{-1} in the cation $(Ru(bipy)_3)^{3+}$ to a ligand field band is unlikely. Also the transition is at lower energy in the ruthenium complex than in the corresponding iron complex, a result which would not be expected for a ligand field band. The half-band-width ($\delta \approx 1200$cm^{-1} in $(Fe(bipy)_3)^{3+}$) is also less than that expected for a ligand field band associated with vibrational structure.

Williams[75] has assigned this band to a ligand field band coupled with a charge transfer band, but the nearest ligand field band would be a much higher energy, and the amount of coupling would be small. Also, Fenske[87] has calculated that ligand field transitions vibronically mix with those ligand to metal charge transfer transitions in which the final states involve the e_g and not the t_{2g} orbital of the metal. The charge transfer transition in this case is $\pi \rightarrow t_{2g}$.

Jorgensen[63] has observed that, in hexahalo complexes, transitions to a t_{2g} level are generally from four to twenty times less intense than those to the corresponding e_g^* level. Even allowing for this the intensity is still low.

There is a marked increase in the intensity in the series iron, ruthenium and osmium. This could suggest the band has some spin-forbidden component. However the intensities of transitions in transition metal complexes are not well understood in many cases, and no conclusions can be drawn.

In the two series of complexes, $(M(bipy)_3)^{3+}$ and $(M(bipy)_2(py)_2)^{3+}$, the energy of the $\pi \rightarrow t_{2g}$ transition is found to increase in the order Ru<Fe<Os. (see Table 7) For the tris complexes the energies are: Ru = 14,790cm^{-1}, Fe = 16,310cm^{-1}, Os = 17,760cm^{-1}. Since the position of the π-orbitals may be expected to change only a small amount on change of metal ion, this energy trend will be one related to the energy of the t_{2g} orbitals.

The relative energy of the t_{2g} orbitals normally (e.g. in hexahalogen complexes[63]) increases in the series 3d to 4d to 5d. However, Gray[61] found that the energy of the first ligand to metal transition is at very similar energies in the hexacyanocomplexes of iron, ruthenium and osmium. Charge transfer data and ionization potential data for the carbonyl complexes of zerovalent (d^6) chromium, molybdenum and tungsten also indicated that the energy of the t_{2g} orbitals remained almost constant in the series 3d→4d→5d.[62] They relate this effect to the strong π-bonding in the complexes. The more diffuse 4d and

5d orbitals are assumed to have more effective overlap with the π*-ligand orbitals. Stronger π-bonding will decrease the energy of the t_{2g} level.

Similar effects seem to be operating in the bipyridyl complexes. The strong π-bonding in the ruthenium complex lowers the energy of the t_{2g} level below that in the iron complex, although the effect of π-bonding is not so marked in the osmium complex. It is interesting that the relative energies of the t_{2g} levels are the same in the trivalent complexes as in the corresponding divalent derivatives (see page 78), although the π-bonding would be expected to be considerably reduced in the trivalent complexes.

The effect of the coordinated ligands (other than bipyridyl) X and Y, (see Table 7) can also be accounted for in terms of the π-bonding ability of the ligand, as for the divalent complexes (see page 77). However, the changes in band energies as the ligand is changed in the trivalent complexes are much less than those in the divalent complexes. This may be related to the reduction in the π-bonding in trivalent compounds.

The band in the cyano-complexes of iron shows a shift to higher energy when bipyridyl is replaced by cyanide (see Fig.20). Cyanide is usually considered to produce a stronger ligand field than bipyridyl, but from the spectral evidence, if π-bonding is a determining factor

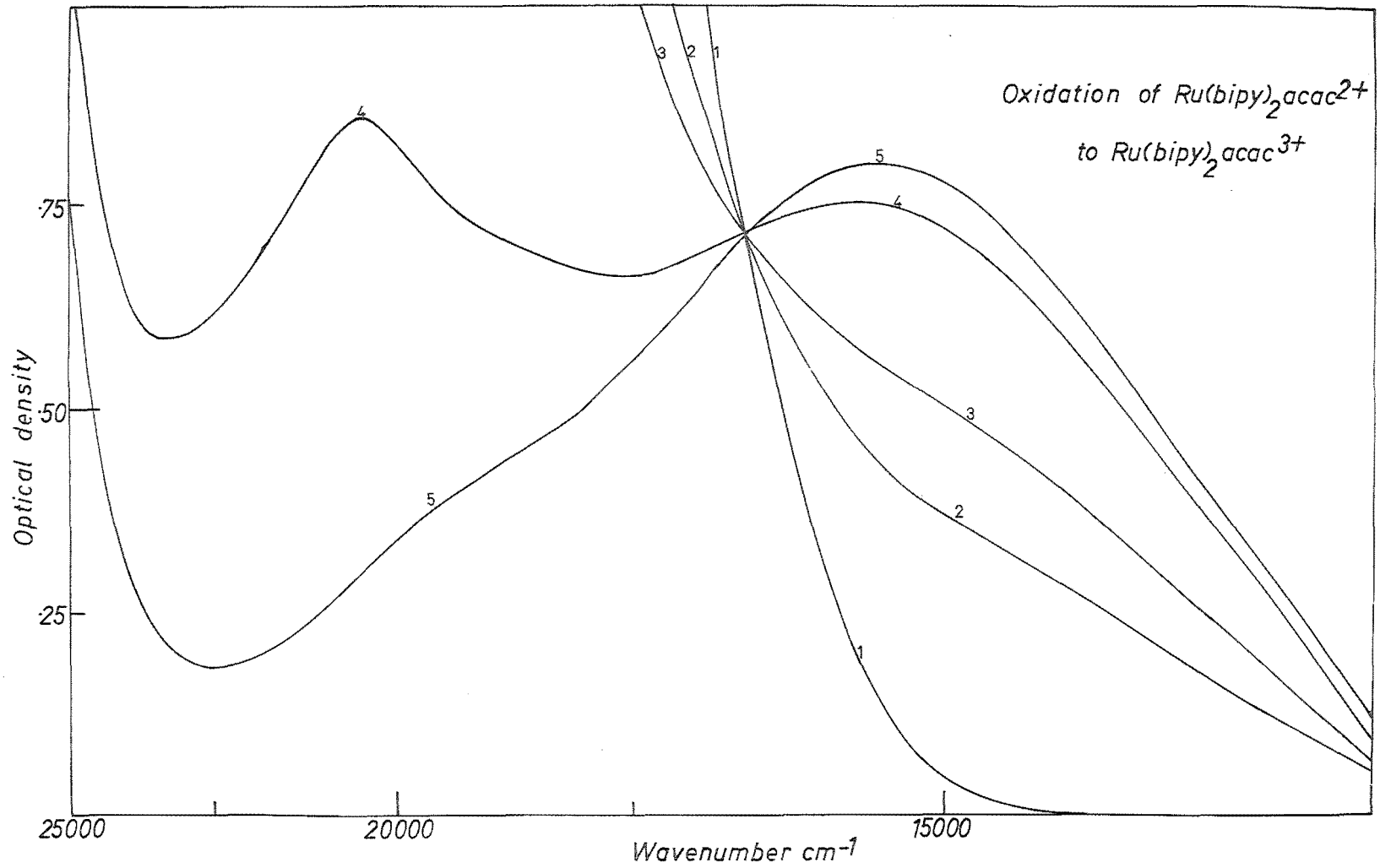
in the t_{2g} energy level, then bipyridyl appears to be a better π-acceptor. However, the effect may perhaps be a consequence of the charge on the cyanide ion. The oxidation potential of the complex $(Fe(bipy)_2(CN)_2)$ moves from -0.781Ev in 0.01 molar sulphuric acid to -0.90Ev in 10 molar sulphuric acid, the reverse of the trend found for the tris-bipyridyl complexes.[23] There is a corresponding small shift in the energy of the $\pi \rightarrow t_{2g}$ transition in the cyano-complexes. The cyanide ligands are assumed to be protonated in strong acid. This will tend to increase the π-back donation and thus stabilise the t_{2g} orbitals, decreasing the energy of the $\pi \rightarrow t_{2g}$ transition. This can be compared with the much larger shifts in the opposite direction observed in the divalent complexes (see page 83).

Other Bands in the Complexes

The osmium complexes all show two small, narrow bands of low intensity ($\varepsilon \approx 10^2$) at ~22,000cm^{-1} which appear as shoulders separated by ~1500cm^{-1} on a rising absorption. It seems likely that they can be assigned to vibrational structure. A band at 25,910cm^{-1} ($\varepsilon < 10^2$) in the iron complex $(Fe(bipy)_3)^{3+}$ may be similarly assigned.

In the complex cation $(Fe(bipy)_2(CN)_2)^+$ a shoulder at 25,320cm^{-1} ($\varepsilon \approx 10^3$) is observed, while in the complex anion $(Fe(bipy)(CN)_4)^-$ there are two strong bands at 24,070cm^{-1}

FIGURE 18


Oxidation of Ru(bipy)2acac2+
to Ru(bipy)2acac3+
Optical density
·75
·50
·25
25000
20000
15000
Wavenumber cm-1
1
2
3
4
5

and 26,600cm^{-1} with intensity $\varepsilon \approx 10^3$. (see Fig.20) They are on the tail of another strong band, but are well resolved, and the band-widths are quite small. The first cyanide to metal charge transfer in the complex $(Fe(CN)_6)^{3-}$ is at 23,500cm^{-1}.[61] It is possible that these bands in the complexes $(Fe(bipy)_2(CN)_2)^+$ and $(Fe(bipy)(CN)_4)^-$ are associated with a similar transition.

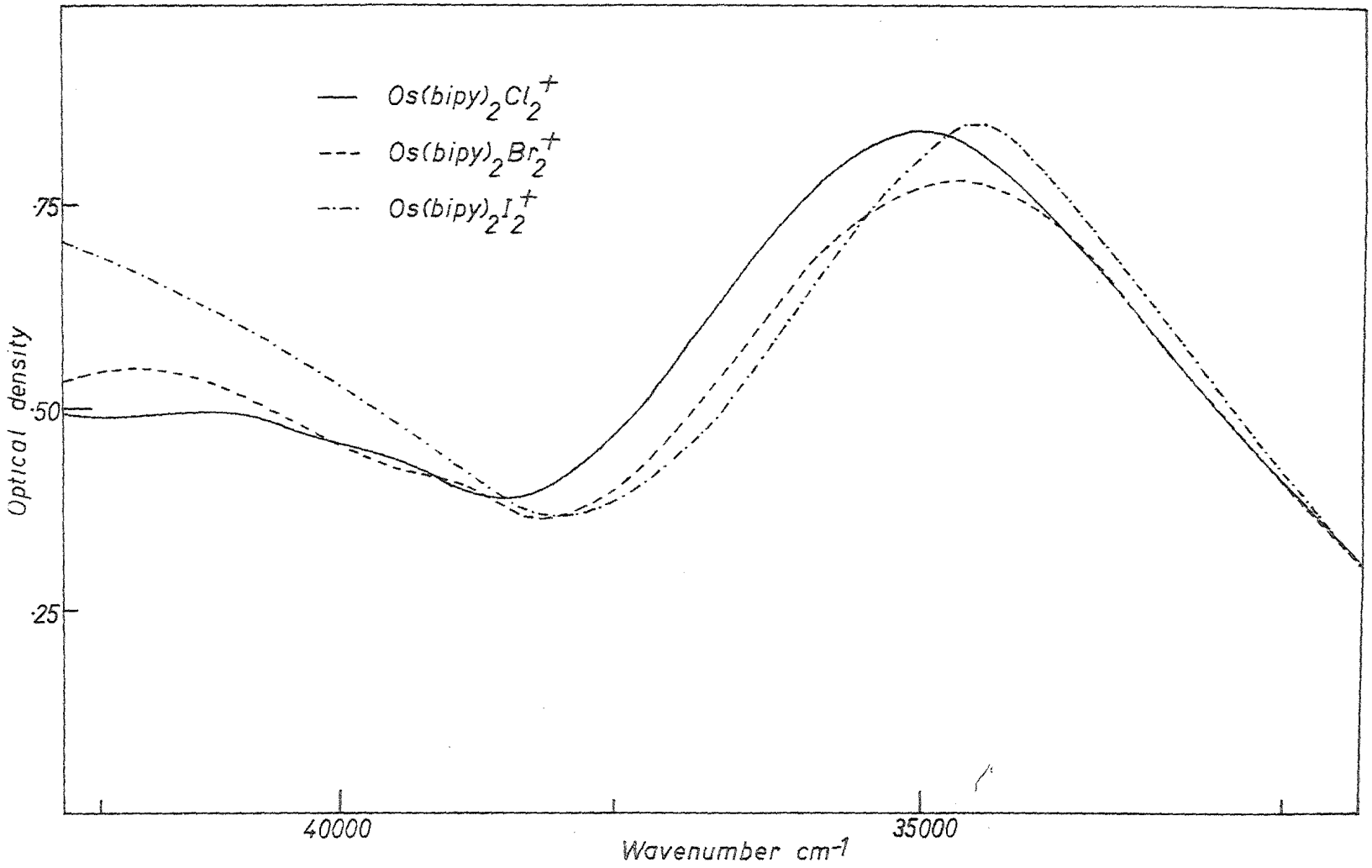
The Complex Cations $(Ru(bipy)_2acac)^+$ and $(Ru(bipy)_2(H_2O)_2)^{3+}$

The ruthenium complex $(Ru(bipy)_2acac)^+$ is the only acetylacetonato-complex to show a spectrum characteristic of the $(M(bipy)_3)^{3+}$ group. (see Fig.18 and Table 9) It shows the characteristic $\pi \rightarrow \pi^*(1)$ transition and also has a band at 15,420cm^{-1} which is assigned as a $\pi \rightarrow t_{2g}$ transition. This band is at higher energy than the one in the tris-complex $(Ru(bipy)_3)^{3+}$ as expected, since bipyridyl is a better π-bonder than acetylacetone. Acetylacetone is also a charged ligand, and the relatively electronegative oxygen atoms will tend to stabilise the trivalent state.

The aquo-ion $(Ru(bipy)_2(H_2O)_2)^{3+}$ also shows a band at 15,100cm^{-1} similar to the $\pi \rightarrow t_{2g}$ transition in the $(M(bipy)_3)^{3+}$ group. However, its intensity is larger than that of the band in $(Ru(bipy)_3)^{3+}$. It is at similar energy to the band in the acetylacetonato-complex, as would be expected, and is probably also a $\pi \rightarrow t_{2g}$ band.

There is also a band at 24,420cm^{-1} (ε=4.07×10^{3}) with a shoulder at 20,920cm^{-1}. This band increases in intensity when ceric ions are added to the solution and may be associated with a ruthenium (IV) impurity. The ultra-violet spectrum is not characteristic of the $(M(bipy)_3)^{3+}$ group. It shows a broad band at 35,030cm^{-1} similar to those found in the acetylacetonato-derivatives to be discussed later. Although the visible spectrum shows some characteristics of the $(M(bipy)_3)^{3+}$ group, this compound is not a representative one. However, this may be due to partial decomposition of the complex in solution (see page 17).

FIGURE 24


Os(bipy)2Cl2+
Os(bipy)2Br2+
Os(bipy)2I2+
·75
·50
·25
Optical density
40000
35000
Wavenumber cm-1

The Bipyridyl Halogeno-Complexes

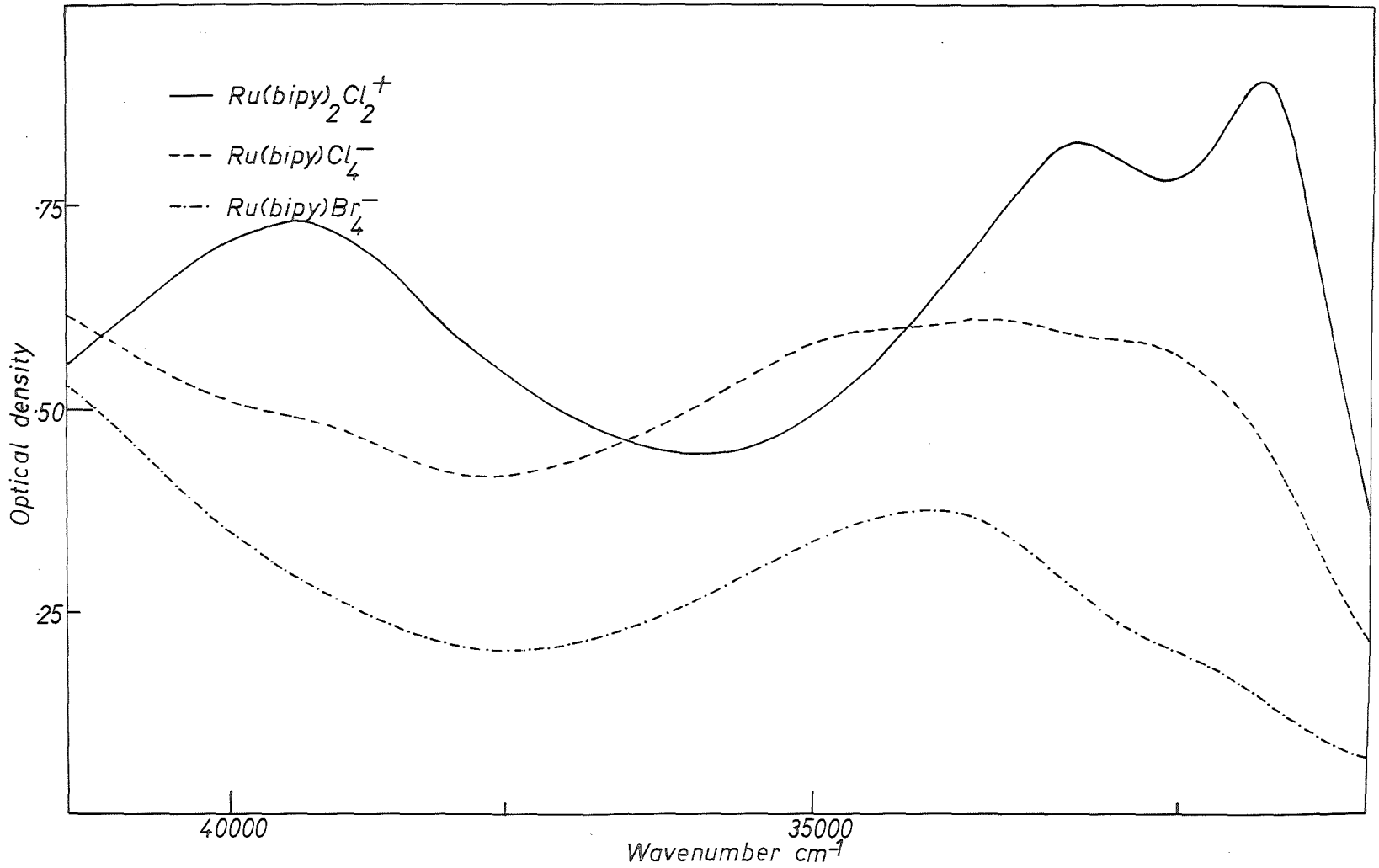
The bipyridyl halogeno-complexes include the complexes of bipyridyl with iron, ruthenium and osmium which contain coordinated halogens. Numerical data for the spectra are given in Table 8, and diagrams of typical spectra in Figs. 23-26.

With the exceptions of the ruthenium complex cation, $(Ru(bipy)_2Cl_2)^+$, and the iron complex $(Fe(bipy)_2Cl_2)(FeCl_4)$, the complexes do not undergo autoreduction in solution (unlike the complexes of the $(M(bipy)_3)^{3+}$ group) and are quite stable in aqueous or alcoholic solutions. The spectra of the complexes in both the visible and ultraviolet regions show considerable differences from those of the $(M(bipy)_3)^{3+}$ group.

Intraligand Transitions

The osmium bipyridyl halogeno-compounds all have very similar ultraviolet spectra. They show the two intraligand bands of bipyridyl, with the lower energy $\pi\rightarrow\pi^*(1)$ transiton at ~34,500cm^{-1} and the other less intense $\pi\rightarrow\pi^*(2)$ transition at higher energy (see Table 8 and Fig.24). The lower energy $\pi\rightarrow\pi^*(1)$ transition is at much higher energy than the transition in the $(M(bipy)_3)^{3+}$ group (see page 91). It also does not show the splitting of the $\pi\rightarrow\pi^*(1)$ transition characteristic of the $(M(bipy)_3)^{3+}$ group, though the band

FIGURE 23


Ru(bipy)2Cl2+
Ru(bipy)Cl4−
Ru(bipy)Br4−
·75
·50
·25
Optical density
40000
35000
Wavenumber cm-1

is broad ($\delta \simeq 2{,}100 cm^{-1}$) and has several shoulders.

The energy of the $\pi \rightarrow \pi^*(1)$ transition increases slightly in the order $(Os(bipy)Cl_4)^- < (Os(bipy)_2I_2)^+ < (Os(bipy)_2Br_2)^+ < (Os(bipy)_2Cl_2)^+$. In the divalent complexes (see page 69) it was found that as the energy of the t_{2g} metal orbital increased, the energy of the $\pi \rightarrow \pi^*(1)$ transition decreased. In these halogeno-complexes, the t_{2g} level is at lowest energy in the complex $(Os(bipy)_2I_2)^+$ (see page 111), and therefore an energy order the opposite of that observed would be expected. It seems here that the ligand producing the strongest field i.e. chloride, causes the highest energy $\pi \rightarrow \pi^*(1)$ transition.

The higher energy $\pi \rightarrow \pi^*(2)$ transition shows energy trends opposite to those of the $\pi \rightarrow \pi^*(1)$ transition.

The spectra of the ruthenium halogeno-complexes are an interesting series. Some of the complexes show spectra typical of the $(M(bipy)_3)^{3+}$ group. The chloro-complex $(Ru(bipy)_2Cl_2)^+$ has two well resolved peaks at $33{,}180 cm^{-1}$ and $31{,}980 cm^{-1}$, with another less intense band at $39{,}440 cm^{-1}$. The pyridine complex, $(Ru(bipy)(py)_2Cl_2)^+$ has two peaks at $32{,}740 cm^{-1}$ and $31{,}510 cm^{-1}$, but the band also has several high energy shoulders. The high energy $\pi \rightarrow \pi^*(2)$ transition at $39{,}290 cm^{-1}$ is more intense than usual.

The complex $K(Ru(bipy)Br_4)$ shows a spectrum very similar to those of the osmium halogeno-complexes. It has

a broad band at 34,110cm^{-1}, with a shoulder at 32,260cm^{-1}, and shows no higher energy $\pi\rightarrow\pi^*(2)$ transition below ~41,000cm^{-1}.

Other complexes have spectra which show features characteristic of both the $(M(bipy)_3)^{3+}$ group and the osmium halogeno-complexes. The complex $K(Ru(bipy)Cl_4)$ shows a very broad flat band with several peaks, which are not well resolved, at 32,740cm^{-1}, 33,710cm^{-1} and 34,600cm^{-1}. There is no $\pi\rightarrow\pi^*(2)$ transition resolved below ~40,000cm^{-1}.

The iron complex, $(Fe(bipy)_2Cl_2)(FeCl_4)$ shows a broad flat band with two badly resolved maxima at 33,590cm^{-1} and 33,010cm^{-1}. The spectrum here may be complicated by bands associated with the $(FeCl_4)^-$ ion.

In the ruthenium series there appears to be a gradual transition from an $(M(bipy)_3)^{3+}$ group type of spectrum to one characteristic of the halogeno-complexes of osmium. As the number of bipyridyl ligands in the complexes is reduced, and as a chloride ligand is replaced by a bromide, (i.e. as the average ligand field strength of the coordinated ligands decreases) the spectra become more like those of the osmium complexes. This is to be compared with the bipyridyl acetylacetonato-complexes (see page 114) where only the ruthenium complex $(Ru(bipy)_2acac)^{2+}$ has the $(M(bipy)_3)^{3+}$ type of spectrum. The visible spectra of the halogeno-complexes are also very different from those of the

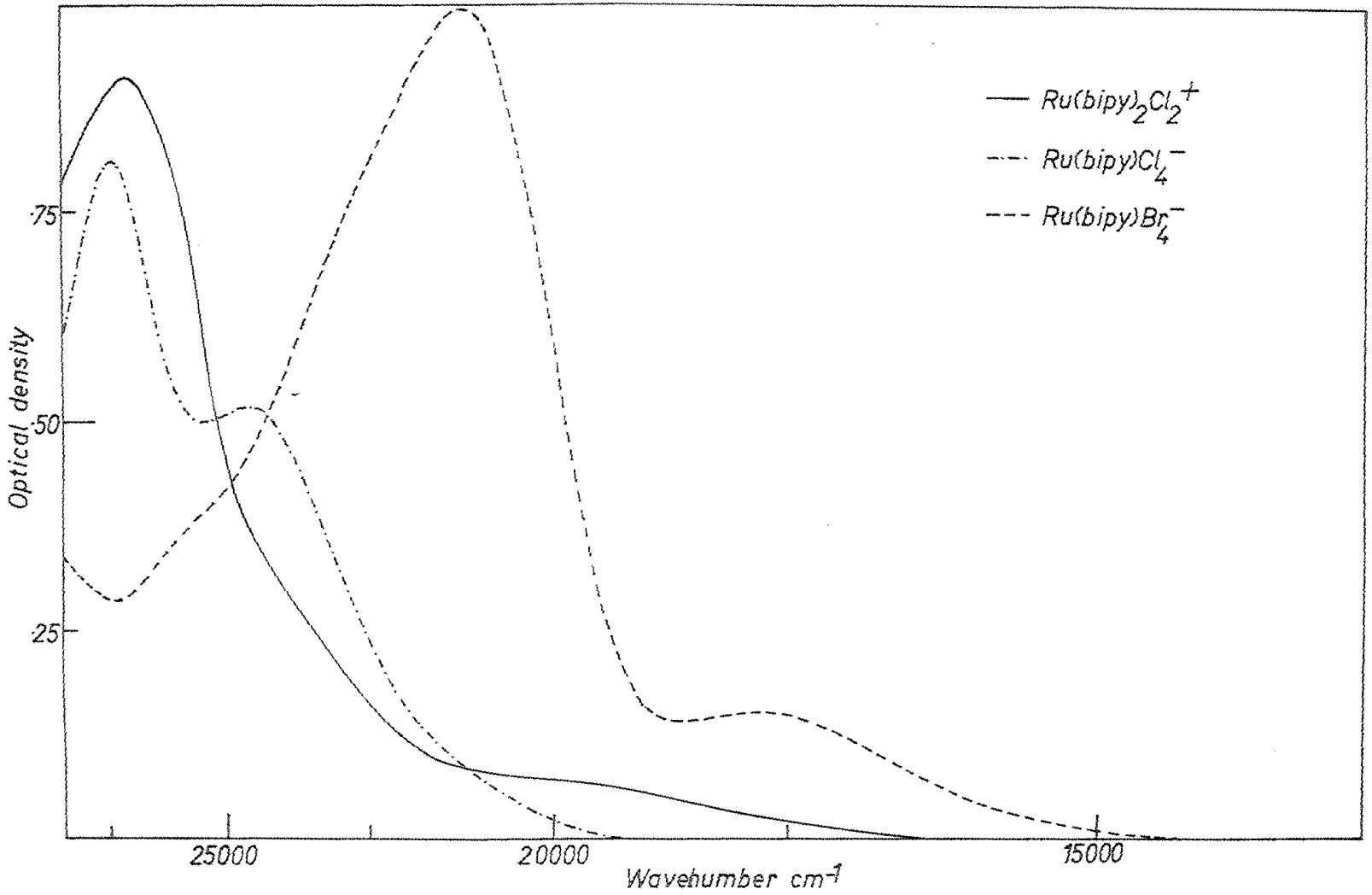
$(M(bipy)_3)^{3+}$ group.

It is interesting that the halogeno-complexes of the cobalt group, $(M'(bipy)_2X_2)^+$ M' = Co,Rh,Ir,[79],[80] show spectra characteristic of the $(M(bipy)_3)^{3+}$ group, as do the tris-bipyridyl complexes of these metals. Therefore whatever is causing the change from the $(M(bipy)_3)^{3+}$ type in the spectrum of the halogeno-complexes is of greatest importance in osmium, then in ruthenium and then in the cobalt group. Weak field ligands also tend to increase the effect. Perhaps this could be related to the relative sizes of the metal bonding orbitals which will have an effect on the overall bond strength.

Those of osmium are more diffuse than those of ruthenium, and orbitals in the cobalt group are generally more contracted than those in the iron group, but as yet no conclusions can be drawn.

It seems unlikely that the spectral changes from the complex $(Os(bipy)_3)^{3+}$ to the chloro-complex $(Os(bipy)_2Cl_2)^+$ are largely related to the effect of the charge on the halogen, since this effect is not observed in the cobalt group complexes. Also the cyano-complexes of iron show typical $(M(bipy)_3)^{3+}$ group spectra. However, Buckingham[28],[29] from a study of the oxidation potentials of osmium halogeno-complexes e.g. $(Os(bipy)_2pyX)^{n+}$, (see page 110) found marked changes in oxidation potential when

FIGURE 25


Ru(bipy)2Cl2+
Ru(bipy)Cl4−
Ru(bipy)Br4−
Optical density
·75
·50
·25
25000
20000
15000
Wavehumber cm-1

for example pyridine was substituted by a halogen, but the reason for these effects is not yet understood.

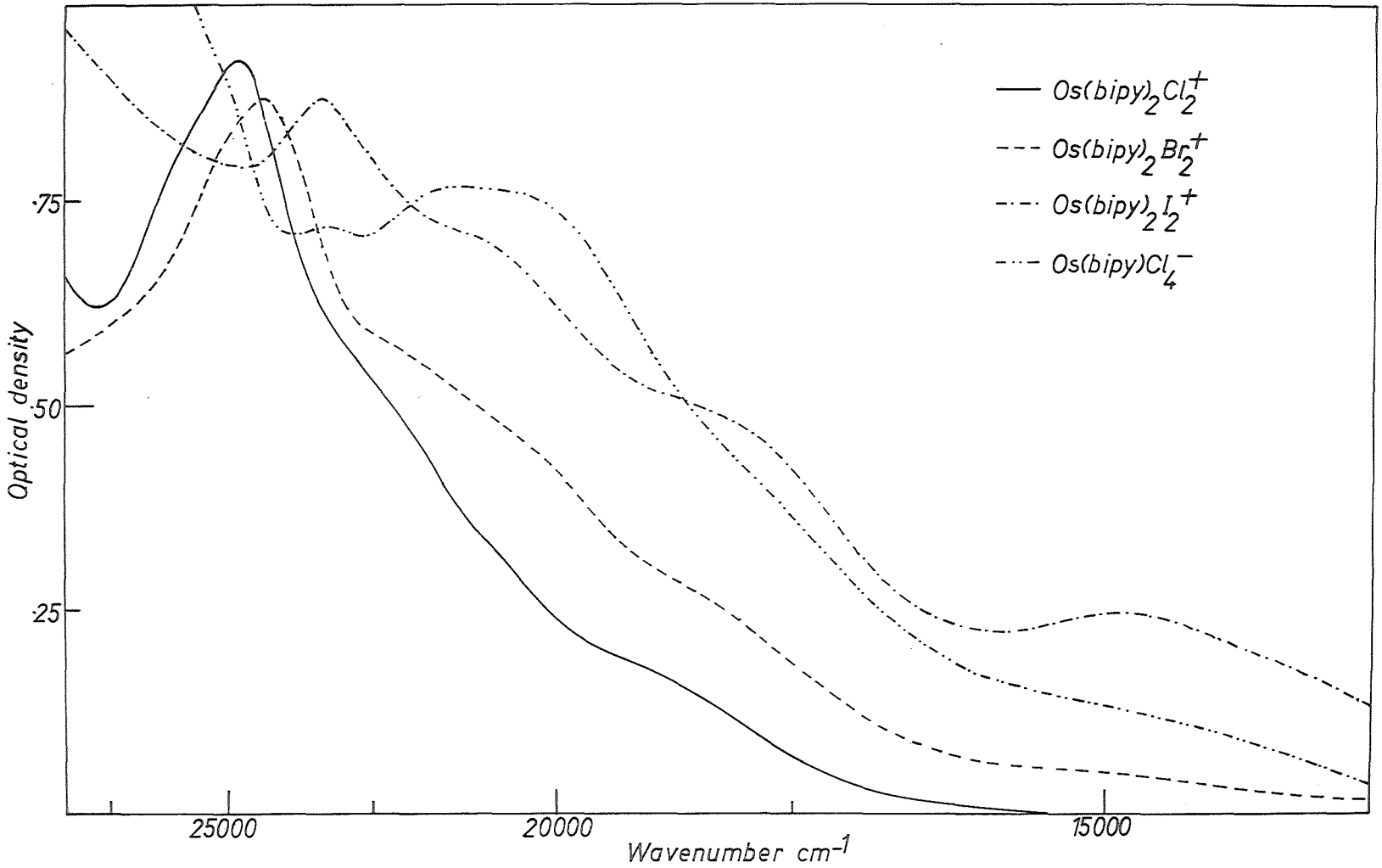
Visible Spectra

The numerical data for the visible spectra of the halogeno-complexes of iron, ruthenium and osmium are given in Table 8. Diagrams of typical spectra are given in Figs.25,26. The spectra of the osmium complexes are different from those of the ruthenium derivatives.

The ruthenium chloro-complexes all have a strong band ($\varepsilon \approx 3\times10^3$) at about 27,500cm^{-1}, with several shoulders to lower energies. In the complex $K(Ru(bipy)Cl_4)$ a shoulder at 24,600cm^{-1} is quite well resolved. The bromo complex, $K(Ru(bipy)Br_4)$ shows a similar spectrum moved to lower energies i.e. a main band at 23,470cm^{-1} and a well resolved shoulder at 17,730cm^{-1}.

In the chloro-complex $(RuCl_6)^{3-}$ the first halogen to metal charge transfer band occurs at 28,650cm^{-1}, while in the corresponding bromide, $(RuBr_6)^{3-}$, it is at 22,500cm^{-1}.[63] The complexes $(Ru(NH_3)_5X)^{2+}$ and $(Ru(NH_3)_4X_2)^{+}$ X = Cl,Br,I, have several bands in the visible and near ultraviolet which are not present in the amine complex $(Ru(NH_3)_6)^{3+}$, and which shift to higher energies in the order I<Br<Cl.[88] Similar bands are found for the corresponding diamine complexes, $(Ru(en)_2X_2)^{+}$ and $(Ru(en)X_4)^{-}$.[89] In the bipyridyl complexes

FIGURE 26


Os(bipy)2Cl2+
Os(bipy)2Br2+
Os(bipy)2I2+
Os(bipy)Cl4−
Optical density
·75
·50
·25
25000
20000
15000
Wavenumber cm-1

the bands are at lower energies than for the amine and halogeno-complexes, but the separation between the band in the bromide complex and in the chloride complex is very similar. The bands are therefore assigned to a halogen to metal t_{2g} charge transfer transition.

The shift of this halogen to metal charge transfer band to lower energies in the bipyridyl complexes relative to the amine and halogen complexes may be explained by stabilisation of the metal t_{2g} orbital by greater π-bonding in the bipyridyl complexes. The shift to higher energies of the band in the complexes $(Ru(bipy)_2Cl_2)^+$ < $(Ru(bipy)(py)_2Cl_2)^+$ < $(Ru(bipy)Cl_4)^-$ may also be explained by the decrease in the importance of π-bonding across the series.

The bipyridyl to metal charge transfer found in the $(M(bipy)_3)^{3+}$ group is not observed in the ruthenium halogeno-complexes. It is possible that it is concealed by the intense halogen to metal transition, but if its position changed only slightly on change of halogen, the large shift in the halogen to metal band from chloride to bromide might be expected to reveal it. However, its intensity may be low, and it may be present only as a shoulder.

The visible spectra of the osmium complexes $(Os(bipy)_2X_2)^+$ X = Cl,Br,I, (see Fig.26) are very different from those of the corresponding ruthenium derivatives. The

spectra are dominated by a strong band at ~24,000cm^{-1} ($\varepsilon \approx 5\times10^3$) which has an overall shift of only 1450cm^{-1} in the series chloride, bromide and iodide. There are also several shoulders to lower energies, and in the case of the iodide there is a band at 14,880cm^{-1} ($\varepsilon = 1.6\times10^3$).

Because the band at 24,000cm^{-1} shifts so little on change of halogen, it is unrealistic to assign it to a halogen to metal charge transfer similar to that found in the ruthenium complexes.

Buckingham[28,29] has published diagrams of the visible spectra of the complexes $(Os(bipy)_2pyX)^{2+}$ and $(Os(bipy)(py)_3X)^{2+}$ X = Cl,Br,I. Unfortunately no numerical data are given, but the spectra are very similar to those found for the complexes $(Os(bipy)_2X_2)^{+}$. They all show a strong band at ~26,000cm^{-1}, though in some cases this is not well resolved. There are also several shoulders to lower energies.

Buckingham[91] has measured the oxidation potentials of the $(Os(bipy)_2pyX)^{+/2+}$ and $(Os(bipy)(py)_3X)^{+/2+}$ X = Cl,Br,I couples. He found they were much less than those of osmium complexes in the $(M(bipy)_3)^{3+}$ group, (where the energy of the bipyridyl to metal charge transfer band has been related to the oxidation potential (see page 96)). For example E_o for $(Os(bipy)_2pyCl)^{+/2+}$ is -0.4823V, while E_o for

$(Os(bipy)_2(py)_2)^{2+/3+}$ is -0.8339V. E_o for the couple $(Os(bipy)_2Cl_2)^{o/+}$ ≃ -0.1V. Thus there is a marked change in the oxidation potential when a halide ion is introduced into the coordination sphere. This effect will in part be related to the different charges on the complexes and related factors.

A study of the ultraviolet spectra of the osmium halogeno-complexes (see page 104) also indicates that the electronic effects in these complexes are different from those in the $(M(bipy)_3)^{3+}$ group. Therefore, although the difference in energy between the bipyridyl to metal ($\pi \rightarrow t_{2g}$) band in $(Os(bipy)_3)^{3+}$ (17,760cm^{-1}) and the band at ~24,000cm^{-1} in $(Os(bipy)_2X_2)^{+}$ is large, it is not unreasonable to also assign the band at ~24,000cm^{-1} to a bipyridyl to metal transition. The band at 26,000cm^{-1} in the pyridine complexes $(Os(bipy)_2pyX)^{2+}$ and $(Os(bipy)(py)_3X)^{2+}$ can be similarly assigned. The intensity of the band is much larger than that of the band in the $(M(bipy)_3)^{3+}$ group, but this could also be a consequence of different electronic structure.

Within the series $(Os(bipy)_2X_2)^{+}$ the shifts of the band on change of halogen can be explained in terms of metal to ligand π-bonding. Iodide, the strongest π-bonder will stabilise the t_{2g} metal orbital more than chloride or bromide. The bipyridyl to t_{2g} transition will therefore be

at lowest energy for the iodide, as observed. The oxidation potentials of the couples $(Os(bipy)_2pyX)^{+/2+}$ and $(Os(bipy)(py)_3X)^{+/2+}$ show a small shift to larger negative values in the series Cl→Br→I.[91] It appears then that the spectral bands show the same trends as the $\pi \rightarrow t_{2g}$ transition in the $(M(bipy)_3)^{3+}$ group i.e. a shift of the band to lower energy as the oxidation potential becomes more negative (see page 96).

In the complex ion $(Os(bipy)_2I_2)^{+}$ there is a band at 14,880cm^{-1} ($\varepsilon \simeq 3\times10^3$). There are also similar bands at ~16,800cm^{-1} in $(Os(bipy)_2pyI)^{2+}$ and at ~16,260cm^{-1} in $(Os(bipy)(py)_3I)^{2+}$. This band is one which is only present in the iodide complexes and is therefore assigned to an iodide to metal charge transfer, similar to those found in the ruthenium halogeno-complexes.

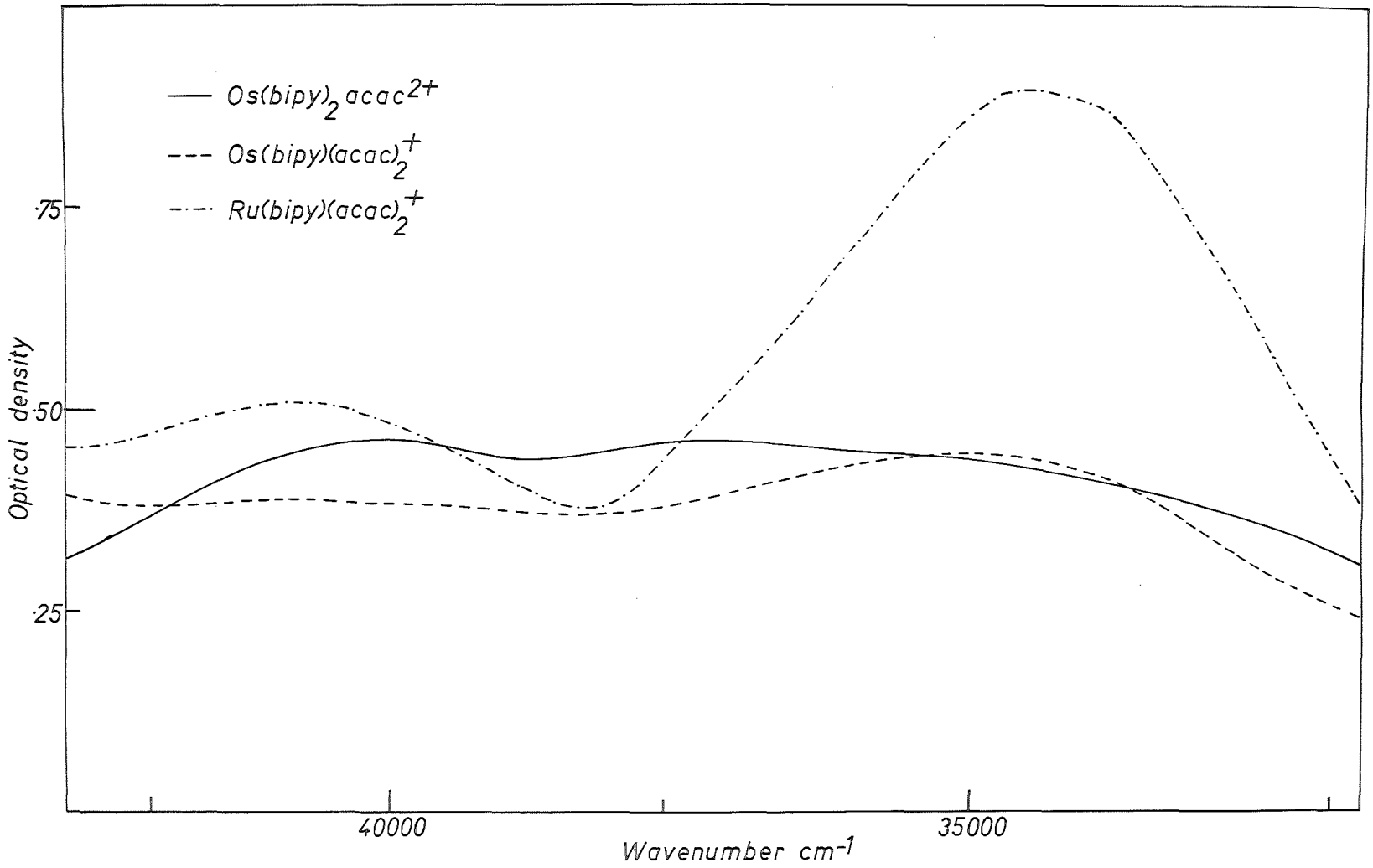
The corresponding halogen to metal bands for the chloro- and bromo-complexes $(Os(bipy)_2X_2)^{+}$, could be concealed by the band at ~24,000cm^{-1}, as there are several shoulders on this band, but the band shape is very similar for both the chloro- and the bromo-complexes, (see Fig.26) and therefore the intensity must be small.

Rather surprisingly, the complex $K(Os(bipy)Cl_4)$ shows a somewhat different visible spectrum from that of the complex $(Os(bipy)_2Cl_2)^{+}$. The spectrum consists of a band

on the side of an absorption which rises to the $\pi \rightarrow \pi^*(1)$ band at 34,230cm^{-1}. This band at ~21,000cm^{-1} also has several shoulders both to lower and to higher energies. It is not possible to assign the band, but it may have the same origins as the bands in the bis-complex $(Os(bipy)_2Cl_2)^+$. The intensity distribution and the energy of the transitions may have altered to give the overlapping bands observed in the complex $K(Os(bipy)Cl_4)$.

The reason for the difference in the spectra for the ruthenium and osmium halogeno-complexes is not yet understood. If the ruthenium complexes do have the bipyridyl to metal charge transfer found in the osmium complexes, or if the osmium complexes have the halogen to metal charge transfer found in the ruthenium complexes, the intensity must be very different in the two metals. It is possible these differences are related to the same effects that are causing the differences in the $\pi \rightarrow \pi^*$ transitions, but it is clear that a better understanding of the spectra is required, perhaps through a more theoretical approach or through studies on similar complexes of other metals, before the problem can be resolved.

FIGURE 27


Os(bipy)2acac2+
Os(bipy)(acac)2+
Ru(bipy)(acac)2+
·75
·50
·25
Optical density
40000
35000
Wavenumber cm-1

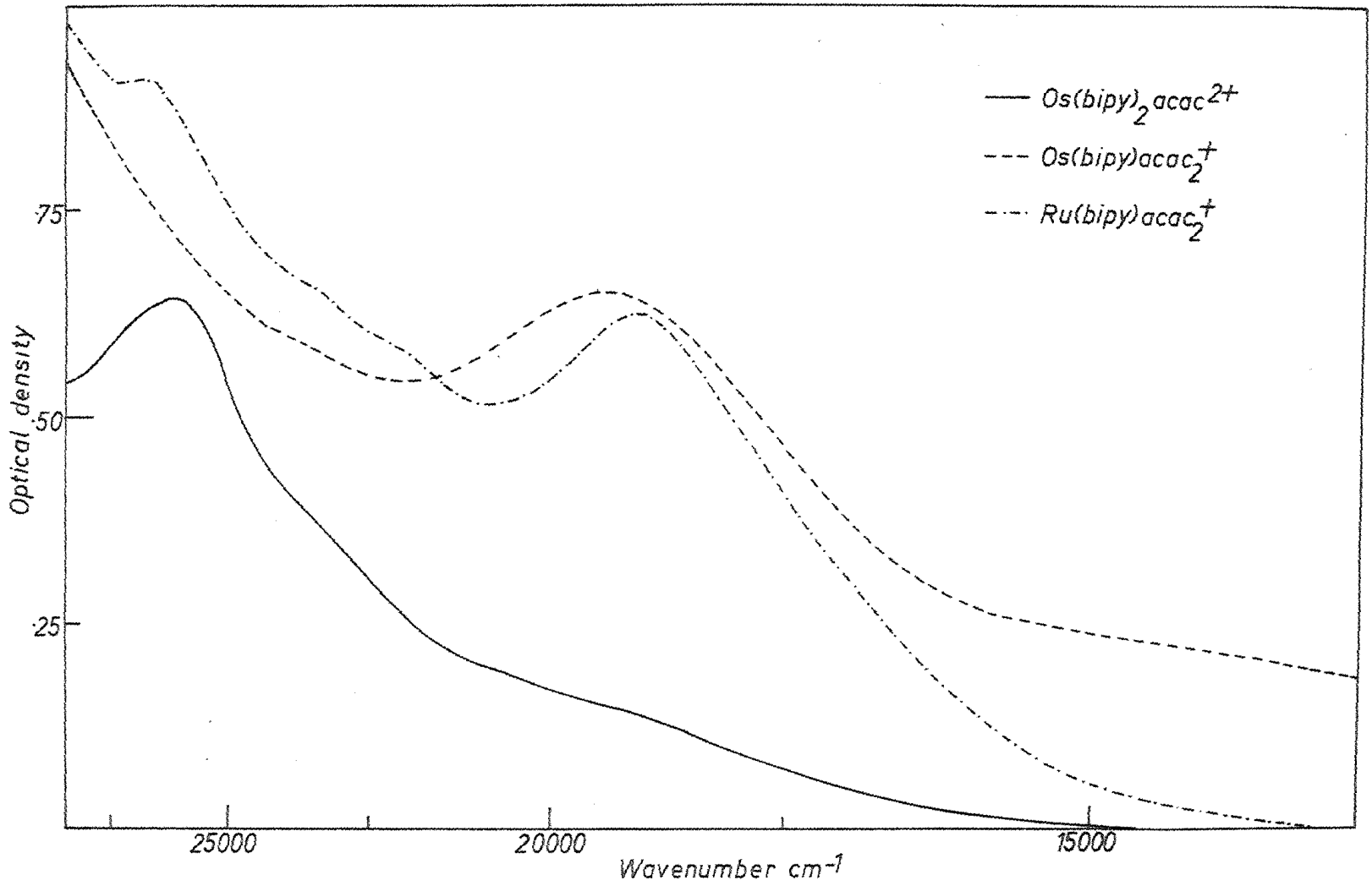
The Bipyridyl Acetylacetonato-Complexes

The bipyridyl acetylacetonato-complexes include the complexes of bipyridyl with trivalent ruthenium and osmium which contain coordinated acetylacetone. The numerical data for the spectra are given in Table 9 and diagrams of the spectra in Figs.18,27 and 28.

The spectra of the acetylacetonato-complexes are difficult to interpret and definite assignments of the bands cannot yet be made. The spectrum of the complex $(Ru(acac)_3)$ has been measured. It shows strong bands at $49,700cm^{-1}$, $37,000cm^{-1}$, $28,600cm^{-1}$ ($\varepsilon \simeq 10^4$ for these bands) and $19,600cm^{-1}$ ($\varepsilon \simeq 10^3$), and tentative assignments have been made. However, these bands may not all occur in the bipyridyl complexes, or they may be at different energies and intensities (see page 73).

Both the osmium complexes show broad, flat absorptions in the ultra-violet region, possibly a result of the overlapping of bands associated with the bipyridyl and acetylacetone ligands. The ruthenium complexes $(Ru(bipy)(acac)_2)^+$ and $(Ru(bipy)acacCl_2)$ show similar spectra, but the bis-bipyridyl complex $(Ru(bipy)_2acac)^{2+}$ has a spectrum typical of the $(M(bipy)_3)^{3+}$ group (see page 102). This can be compared with the chloro-complexes where

FIGURE 28


Os(bipy)$_2$acac^{2+}
Os(bipy)acac$_2^+$
Ru(bipy)acac$_2^+$
Optical density
.75
.50
.25
25000
20000
15000
Wavenumber cm^{-1}

$(Ru(bipy)_2Cl_2)^+$ and $(Ru(bipy)(py)_2Cl_2)^+$ are the only halogeno-complexes to show ultraviolet spectra typical of the $(M(bipy)_3)^{3+}$ group.

In the visible region, the complex $(Os(bipy)_2acac)^{2+}$ shows a band at 26,040cm^{-1} with several shoulders to lower energy. The complex $(Os(bipy)(acac)_2)^+$ has a band at 19,310cm^{-1} on the side of an intense ultraviolet absorption. The spectrum extends to much lower energies than in $(Os(bipy)_2acac)^{2+}$, and there is a shoulder at ~11,000cm^{-1}.

It is unlikely that the bands at 19,310cm^{-1} in the complex $(Os(bipy)(acac)_2)^+$ and at 26,040cm^{-1} in the complex $(Os(bipy)_2acac)^{2+}$ can both be assigned to a metal reduction transition. From oxidation potential data it has been found that acetylacetone stabilises the trivalent state.[91]

$$E_o(Os(bipy)_2acac)^{+/2+} = -0.1539V,$$

$$E_o(Os(bipy)_3)^{2+/3+} = -0.8836V$$

The stabilisation of the trivalent state would be expected to be even greater in $(Os(bipy)(acac)_2)^+$. Therefore any metal reduction spectra would be expected to be at higher energies in the complex $(Os(bipy)(acac)_2)^+$ than in the complex $(Os(bipy)_2acac)^{2+}$. The two bands in this case show the opposite trend.

The spectrum of the complex $(Ru(bipy)(acac)_2)^+$ is very similar to that of the osmium complex $(Os(bipy)(acac)_2)^+$. except for an additional shoulder at 26,740cm^{-1}. In the spectrum of the chloro-complex $(Ru(bipy)(acac)Cl_2)$ there are a number of additional absorptions. One at 28,270cm^{-1} may be a halogen to metal transition (see page 109). Another at 16,640cm^{-1} is similar to the band at 15,420cm^{-1} in the complex $(Ru(bipy)_2acac)^{2+}$, but the assignment is uncertain.

It can therefore be seen that the spectra of these acetylacetonato-compounds are somewhat more complex than those of the $(M(bipy)_3)^{3+}$ group or the halogeno-complexes, and that definite assignments of the bands are not yet possible.

TABLE 7

SPECTRA OF THE TRIVALENT COMPLEXES OF THE $(M(bipy)_3)^{3+}$ GROUP

Complex and Solvent	(a)	$\pi\rightarrow\pi^*(2)$	$\pi\rightarrow\pi^*(1)$				$\pi\rightarrow t_{2g}$
$(Fe(bipy)_3)^{3+}$	ν		32870	31730	25910[b]		16310
H_2O/Cl_2	ε		34100	34000	<100		289
	δ			730			1240
$(Fe(bipy)_2(CN)_2)^{+}$	ν		33050	32020	25320[c]		18220
3N HCl	ε		22900	22800	~1180		194
	δ			870			1180
$(Fe(bipy)(CN)_4)^{-}$	ν	(40980)	33580	32260	26600[c]	24070[c]	19690
H_2O/Cl_2	ε		11300	13050	1310	895	104
	δ			450		790	1770
$(Ru(bipy)_3)^{3+}$	ν						14790
H_2O/Ce^{4+}	ε						409
	δ						1240
$(Ru(bipy)_2(py)_2)^{3+}$	ν						14800
H_2O/Ce^{4+}	ε						261
$(Ru(bipy)(py)_4)^{3+}$	ν						14730
H_2O/Ce^{4+}	ε						150

(Cont.)

TABLE 7 (Continued)

$(Ru(bipy)_2acac)^{2+}$	ν	40500		33310	32010				15420
H_2O/Ce^{4+}	ε	33200		29300	28000				1126
$(Ru(bipy)_2(H_2O)_2)^{3+}$	ν	42830		35030			24420	(20920)	15100
	ε	19750		24600			4070		6020
	δ			3020					1070
$(Os(bipy)_3)^{3+}$	ν	40390		32590	31640		23390[b]	21830[b]	17760
3N HCl	ε	50100		39200	42200		<100	<100	585
	δ				780				1310
$(Os(bipy)_2(py)_2)^{3+}$	ν	38670		32540	31520		23530[b]	21860[b]	18120
3N HCl	ε	27000		18500	20500		<100	<100	396
	δ				740				1530
$(Os(bipy)_2phen)^{3+}$	ν	(40950)	36660[d]	32790	31630	(25710)	23420[b]	22170[b]	17830
3N HCl	ε		46600	33600	32250		<100	<100	808
	δ				900				1770
$(Os(4,4'\text{-diMebipy})_3)^{3+}$	ν	39450		33070	31930	(28150)		21910[b]	18640
3N HCl	ε	53200		38700	41500				603
	δ								1560

Values in parenthesis indicate shoulders.

(Cont.)

TABLE 7 (Continued)

(a) ν = band energy in cm^{-1}, ε = extinction coefficient in $Moles^{-1}cm^{-1}$, δ = half-band-width in cm^{-1}.

(b) Vibrational Structure.

(c) CN^- → metal charge transfer.

(d) Intraligand transition of 1,10-phenanthroline.

TABLE 8

SPECTRA OF THE TRIVALENT BIPYRIDYL HALOGENO-COMPLEXES

Compound and Solvent	(a)	$\pi\rightarrow\pi^*(2)$			$\pi\rightarrow\pi^*(1)$		$X\rightarrow t_{2g}$		$\pi\rightarrow t_{2g}$			
$(Fe(bipy)_2Cl_2)^+$	ν				33590	33010	27400					16950
CH_2Cl_2	ε				31300	31200	11150					~60
	δ						2240					
$(Ru(bipy)_2Cl_2)^+$	ν	39440			33180	31980	27030			(23530)	(19230)	
3NHCl	ε	23250			26400	28100	4700				340	
						620	2060					
$(Ru(bipy)(py)_2Cl_2)^+$	ν	39290	(38270)	(33640)	32740	31510	28050	(26460)		(22080)	(17790)	
3NHCl	ε	21300			12100	12400	2720				<100	
$(Ru(bipy)Cl_4)^-$	ν			34600	33710	(32740)	27430	24600				
H_2O	ε				12400		3860	2680				
$(Ru(bipy)Br_4)^-$	ν				34110	32260	23470	17730		(25640)		
H_2O	ε				18350		4830	792				
$(Os(bipy)_2Cl_2)^+$	ν	41010			34740				24810	(22220)	(19050)	
	ε				28800				5060			
	δ				2470							

(Cont.)

TABLE 8 (Continued)

$(Os(bipy)_2Br_2)^+$	ν	41670	34480			24360	(21100)	(18080)	
$(Os(bipy)_2I_2)^+$	ν		34330	14880		23360	(20700)	(18180)	
$(Os(bipy)Cl_4)^-$	ν	41290	34230		(26530)		(23200)	21230	(17860)
	ϵ	10700	20470					1900	

Values in parenthesis indicate shoulders.

(a) ν = band energy in cm^{-1}, ϵ = extinction coefficient in $Moles^{-1}cm^{-1}$,
δ = half-band-width in cm^{-1}.

TABLE 9

SPECTRA OF THE TRIVALENT BIPYRIDYL ACETYLACETONATO-COMPLEXES

Compound and Solvent	(a)								
$(Ru(bipy)_2acac)^{2+}$	ν	40500		33310	32010				15420
H_2O/Ce^{4+}	ε	33200		29300	28000				1126
$(Ru(bipy)(acac)_2)^{+}$	ν	40880		34620	(34000)	26740		19050	
MeOH	ε	16700		29200				2860	
$(Ru(bipy)acacCl_2)$	ν			34340		28270	20990	19820	16640
CH_2Cl_2	ε			22700		6020	1590	1430	685
$(Os(bipy)_2acac)^{2+}$	ν	40000 (b)	37950 (b)	35310 (b)		26040	(24210)	(19800)	
H_2O	ε	22500	22200	21200		4610			
$(Os(bipy)(acac)_2)^{+}$	ν	40980 (b)		35020				19310	~12000
MeOH	ε			25850				7360	<100

Values in parenthesis indicate shoulders.

(a) ν = band energy in cm^{-1}, ε = extinction coefficient in $Moles^{-1}cm^{-1}$

(b) Broad band.

CHAPTER V

ELECTRONIC ABSORPTION SPECTRA OF BIPYRIDYL COMPLEXES OF OTHER METALS

In this chapter, the spectra of bipyridyl complexes with other metals are briefly reviewed, and the results related to those obtained in the present work. Unfortunately many bipyridyl complexes known, particularly those of second and third row transition metals, are polynuclear derivatives or in the case of e.g. platinum and palladium square planar. There is also some evidence that the numerous complexes with low metal oxidation states contain the $(bipy)^-$ anion. It is difficult to compare the spectra of these types of complexes with those of the monomeric "octahedral" derivatives discussed in the present work, and therefore they will not be considered further.

The amount of spectroscopic data for simple "octahedral" type bipyridyl complexes in the literature is limited. Often the data are incomplete or do not agree with the results obtained by other workers. Recently, however, there has been considerable interest shown in related fields, such as circular dichoism e.g.[53,70,71] and luminescence e.g.[84,92].

The ligand field spectra of a number of complexes of bipyridyl with metals such as chromium[71,94], cobalt[71,76,94,95,96], rhodium[79,80], nickel[53,97,76] and copper[76] have been studied. The bands show the expected trends, i.e. complexes containing strong field ligands other than bipyridyl in the coordination sphere have bands at higher energies than those containing weak field ligands. The ligand field parameters calculated indicate considerable participation of the π-electrons in bonding.[76]

Intraligand Transitions

The ultra-violet spectra of bipyridyl complexes show the strong intraligand transitions of bipyridyl. In the spectra of the tris-bipyridyl complexes of the divalent metals of the first transition series there is a shift to lower energies of the lower energy $\pi \rightarrow \pi^*(1)$ transition of bipyridyl for the series $Mn^{2+} \rightarrow Zn^{2+}$.[69,98] Gil et al[69] have predicted this from a qualitative theoretical approach. A shift to lower energy of the $\pi \rightarrow \pi^*(1)$ band as the charge on the metal ion is increased has also been observed, e.g. for $Co^{+} \rightarrow Co^{2+} \rightarrow Co^{3+}$ [69] and for $Fe^{2+} \rightarrow Fe^{3+}$ (in the present work). It has been suggested[98] that the energy of the band is largely dependant on electrostatic interaction, as discussed on page 67. There are a number of exceptions to this trend. These include the bipyridyl halogeno-

complexes of ruthenium (III) and osmium (III) (see page 104), chromium (III) complexes and the technetium complexes $(Tc(bipy)_2Cl_2)^{2+}$ and $(Tc(bipy)Cl_4)$,[99] all of which have the $\pi\rightarrow\pi^*(1)$ band at an energy very close to that for free bipyridyl. It is unfortunate that there is not more data available which would assist in determining the relevant factors for the energy of this band.

Other than in the present work there is little data available on the effects of changing the coordinated ligand, X, in a series of complexes of the type $(M(bipy)_2X_2)^{n+}$. Vlcek[95] and Aprile and Maspero[96] have reported the spectra of a number of bis-bipyridyl cobalt (III) complexes. They found the intraligand spectra were generally similar to those of the $(M(bipy)_3)^{3+}$ group discussed in the present work (see page 92) but in some cases e.g. X = OAc^-, CO_3^{2-}, instead of two bands, there was only a single absorption. This may be compared with the situation in the ruthenium (III) halogeno-complexes (see page 105), where weak field ligands tended to give rise to single bands. Although it is difficult to make definite deductions from the published spectra, it does appear that the $\pi\rightarrow\pi^*(1)$ bands are at higher energy in complexes containing weak field ligands, X.

The approximate energy order is

$I^- \approx H_2O > Br^- >$ bipy $\approx NO_2^-$. This is to be contrasted with the situation in the iron group compounds (see Chapters III and IV) where strong field ligands cause a shift of the bands to higher energies. In the rhodium (III) and iridium (III) complexes, there is very little change in band energy in the series bipy→Cl→Br→I.

Ferguson et al have published spectral data for chromium (III)[71] complexes and nickel (II)[53] complexes. In the chromium series $(Cr(bipy)(C_2O_4)_2)^-$, $(Cr(bipy)_2C_2O_4)^+$, $(Cr(bipy)_3)^{3+}$ there appears to be a slight shift in the $\pi\rightarrow\pi^*(1)$ band to lower energy as the ligand field strength of the coordinated ligands increases, the reverse of the effect found for the iron group complexes. In the nickel complexes any shifts appear to be small, and the effects in both cases can be accounted for in terms of vibrational and other interactions.

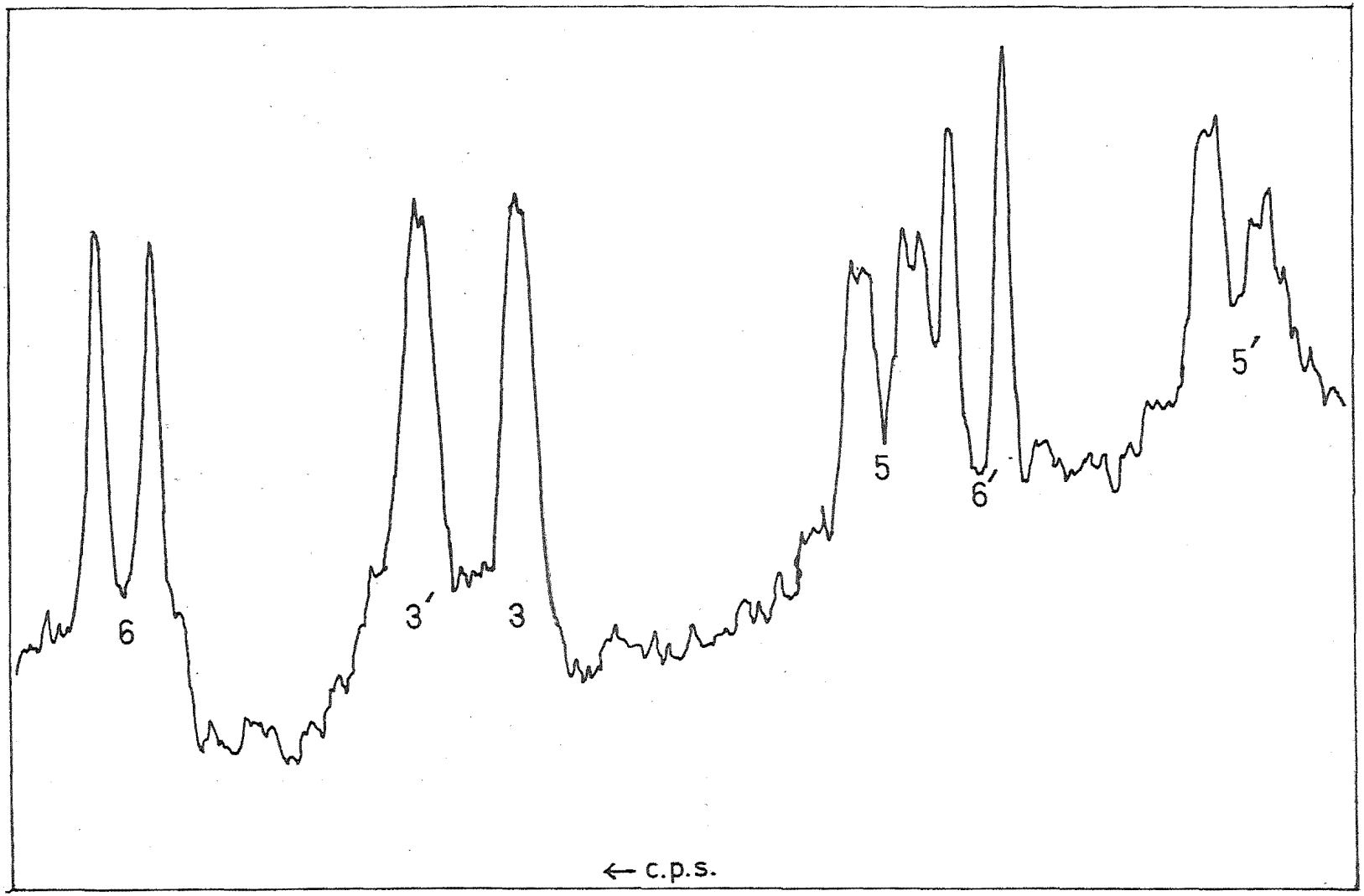
Charge Transfer Transition

The strong charge transfer bands found for the iron group complexes are observed in very few other bipyridyl complexes of transition metals. Vlcek[95] has reported a band at ~23,000cm^{-1} to ~26,000cm^{-1} in some cobalt (III) complexes which he has assigned to a charge transfer transition. The $\pi\rightarrow t_{2g}$ transition found in the $(M(bipy)_3)^{3+}$

group of complexes (see Chapter IV) will not be possible in these $(t_{2g})^6$ complexes, and the energy is rather low for either a $\pi \rightarrow e_g^*$ (metal reduction) transition or a $t_{2g} \rightarrow \pi^*$ (metal oxidation) transition. A similar band is not found in the bipyridyl halogeno-complexes of rhodium and iridium, and a definite assignment of the band is not therefore possible.

Manganese (II) does not show any charge transfer bands in the visible, unlike the spin-free iron (II) complexes. Metal oxidation bands would be expected at lower energies for manganese (II) than for iron (II).[61] Chromium (III) complexes have a shoulder on the lower energy side of the $\pi \rightarrow \pi^*(1)$ absorption,[71] but this has not been assigned. Nickel (II) complexes have been reported to show charge transfer bands at ~25,000cm^{-1},[97] but these bands have not been studied. Charge transfer bands have also been reported for cobalt (I), rhodium (I) and silver (I) derivatives but the composition of these complexes is uncertain. It is clear that further and more detailed spectroscopic and related studies are necessary to resolve many of the problems and inconsistencies associated with the charge transfer spectra of bipyridyl complexes.

FIGURE 29



NMR of $Ru(4,4'\text{-diMebipy})_2(NH_3)_2^{2+}$

CHAPTER VI

PROTON MAGNETIC RESONANCE SPECTRA OF DIVALENT COMPLEXES

The proton magnetic resonance spectra of several complexes of 4,4'-dimethylbipyridyl with iron (II), ruthenium (II) and osmium (II) are reported and discussed in this chapter. The range of complexes studied is limited since most of the 4,4'-dimethylbipyridyl complexes are not sufficiently soluble, even in such solvents as dimethyl-sulphoxide, to enable an NMR spectrum to be obtained even by the use of a time averaging computer (CAT)(see page 133).

The NMR spectra of 4,4'-dimethylbipyridyl complexes (e.g. see Fig.29) are in general readily analysed. Ignoring couplings of less than ~2 c.p.s the 3-proton (see Fig.1) generally gives a single peak, which has some fine structure which is not resolved. Protons 5 and 6 give rise to a characteristic AB type of spectrum, consisting of two doublets. One pair of peaks is smooth and sharp, showing little fine structure, but the other is broader, and the peaks are similar in appearance to that of the 3-proton. This second pair which is assigned to the 5-proton has been split by the adjacent methyl group in the 4-position. Therefore for each pyridine ring of the ligand five peaks are to be expected, one of which will have a greater integrated intensity. When all the pyridine rings

are equivalent, e.g. as in the tris complexes, the spectrum will show only five peaks.

The main peaks for the spectra of the complexes are given in Table 11. The resonance frequencies are given in cycles per second and in parts per million from tetramethylsilane. Table 12 gives the proton resonances and coupling constants (in cycles per second) obtained after analysis of the 5- and 6-proton peaks in terms of an AB system.

The resonance of the 4-methyl group in the 4,4'-dimethyl bipyridyl complexes was not obtained, as in methanol solution the position of this peak is either concealed or the assignment complicated by the presence of solvent side-bands.

Castellano et al[100] have studied the spectrum of bipyridyl in a variety of solvents and the spectrum of the iron complex $(Fe(bipy)_3)^{2+}$. They found that, relative to bipyridyl in proton donor solvents, only the chemical shift of proton 4 remained unchanged in the iron complex. Proton 3 of coordinated bipyridyl was shifted downfield by 0.85 p.p.m. and protons 5 and 6 were shifted upfield by 0.16 p.p.m. and 1.28 p.p.m. respectively. The 3-,3'-protons lie very close to each other and Van der Waals forces contribute substantially, together with the anisotropic effect of ring current to the observed deshielding. Good agreement with calculations has been obtained. Proton 6

lies close to and above the plane of the pyridine ring of a second ligand group. The reason for the large upfield shift of this proton is thereby clear. The magnetic anisotropy of the same pyridine ring is also responsible for the shift toward higher fields of the resonance of proton 5.

The tris 4,4'-dimethylbipyridine derivatives should show similar spectra modified by the methyl substituent. The introduction of an electron donating group, such as a methyl group, into an aromatic ring gives rise to a change in the shielding constants of the protons, causing the proton resonances to shift toward higher fields.[101] This is observed in the present work for 4,4'-dimethylbipyridyl complexes. For comparison, the spectra of several unsubstituted bipyridyl compounds were measured, but owing to the complexity of the spectra accurate assignments of the resonance frequencies were not made. However, the estimated values indicated that the resonances are all shifted (~15 c.p.s.) upfield in the 4,4'-dimethylbipyridyl complexes relative to the bipyridyl complexes.

N.M.R. of the tris-(4,4'-dimethylbipyridyl) complexes.

The spectrum of the complex $(Fe(4,4'\text{-diMebipy})_3)^{2+}$ in methanol shows only two bands with an intensity ratio of 1:2. The spectrum of the complex $(Fe(bipy)_3)^{2+}$ has been studied and assigned,[100] and by comparison with this it is

possible to assign the less intense resonance at 522 c.p.s. to proton 3. Protons 5 and 6 have now become equivalent, and show only the single, rather broad, band at 444 c.p.s.

For the complex $(Ru(4,4'\text{-diMebipy})_3)^{2+}$ the characteristic five peak pattern is observed. Proton 3 is at lower field than the 5-, 6-proton doublets. The doublet at lower field is sharp and smooth and is assigned to proton 6. The complex $(Os(4,4'\text{-diMebipy})_3)^{2+}$ shows a very similar spectrum.

In the series iron to ruthenium to osmium for the tris complexes, there is a shift of proton 3 to higher field. Somewhat similar effects are observed for protons 5 and 6. The shifts will be influenced by the anisotropic effect of adjacent pyridine rings, which will vary with the metal-nitrogen bond distance. The estimated covalent radii of the bivalent metal ions are 1.23Å, 1.33Å, 1.33Å respectively for iron, ruthenium and osmium, while the covalent radius for nitrogen is 0.74Å.[102] Castellano et al[100] have calculated the shieldings caused by the adjacent pyridine ring of protons 5 and 6 for several metal nitrogen distances. As the bond length decreases, there is a shift toward higher field of the protons. Their calculated values are;

D_{M-N}(Å)	Shielding of proton 5 (p.p.m.)	Shielding of proton 6 (p.p.m.)
1.97	.30	1.37
2.04	.27	1.12

If allowance is made for this effect (i.e. the observed chemical shifts of the iron complexes are adjusted to make allowance for the decreased metal-nitrogen distance in the iron complex compared to that in the ruthenium and osmium complexes) chemical shifts for the tris complexes which are now less influenced by steric effects are obtained. These chemical shifts show a general shift toward higher field in the series iron, ruthenium and osmium for the tris-(4,4'-dimethylbipyridyl) complexes. This upfield shift can be explained in terms of metal to ligand π-bonding.

The changes in proton resonances on the introduction of a substituent into an aromatic ring have been interpreted as arising from changes in the π-electron density at the carbon atoms, and it has been suggested that the shift is directly proportional to the change in the π-electron charge density, though other effects may also be important.[101] In a metal ion complex, the metal ion could perhaps be compared with a substituent in the ring. π-bonding between the metal ion and a ligand such as bipyridyl will tend to increase the electron density in the ring, causing a shift

to higher fields (σ-bonding would operate in the opposite direction). In the tris complexes of iron, ruthenium and osmium effects related to the shape of the molecule, ring currents etc. should be reasonably constant. Therefore the shift to higher field of the proton resonances in the series iron to ruthenium to osmium could be explained in terms of increasing π-bonding. Spectroscopic evidence presented in Chapters III and IV indicates the much greater importance of π-bonding in ruthenium than in iron, though the evidence for an increase from ruthenium to osmium is less certain.

N.M.R. of the iron complex, $(Fe(4,4'\text{-diMebipy})(CN)_4)^{2-}$

The spectrum of the iron complex, $(Fe(4,4'\text{-diMebipy})(CN)_4)^{2-}$ shows the five peak pattern, but in this case proton 6 is shifted to much lower field and proton 3 to higher field relative to the tris-complex. The downfield shift of proton 6 can be explained by the anisotropic effect of the C ≡ N triple bond in the adjacent cyanide ligand. The reason for the large shift in proton 3 is less certain, since it is unlikely to be the result of anisotropy of a neighbouring group. However, it could be related to the polar nature of the molecule compared to the tris-complex.

N.M.R. of the bis-(4,4'-diMethylbipyridyl) ruthenium complexes.

The spectra of two bis(4,4'-diMethylbipyridyl) complexes of ruthenium, $(Ru(4,4'\text{-diMebipy})_2(NH_3)_2)^{2+}$ and $(Ru(4,4'\text{-diMebipy})_2acac)^{+}$, have been measured. They show two sets of five peaks (see Fig.29), which indicates that the two pyridine rings of the bipyridyl ligand are not equivalent. This is evidence for the cis-configuration of the complexes (see Fig.4) since in the trans-configuration all the pyridine rings would be in the same environment and would thus be equivalent. The spectrum would then consist of only five resonances.

Assignment of the peaks in the bis-(4,4'-dimethylbipyridyl) ruthenium complexes is somewhat more difficult than in the mono- and tris- complexes. In the ammonia complex (see Fig.29), the 3- and 3'- protons can be assigned to two somewhat broadened peaks at 500.8 c.p.s. and at 511.6 c.p.s. The four sets of doublets can readily be assigned to the 5,6- and the 5',6'- protons. However it is difficult to determine which of the pyridine rings making up the ligand the resonances are associated with. One ligand pyridine ring will be trans to the nitrogen of the pyridine ring of the other 4,4'-dimethylbipyridine ring, while the other ligand pyridine ring will be trans to an ammonia ligand (see Fig.4). For the pyridine ring trans

to the pyridine ring of the second ligand the 6 (and 5) proton will not be directly above the plane of another pyridine ring, and will therefore not be subject to the anisotropic effect which causes a shift to higher field of the 5 and 6 protons in the tris complexes. Therefore the resonances at 544.3 c.p.s. and 460.6 c.p.s. may be assigned to the 6 and 5 protons in this ring. The resonances at 421.7 c.p.s. and 450.4 c.p.s. are therefore assigned to the 5' and 6' protons in the ring trans to the ammonia ligands. These protons will be affected by the anisotropic effect of the neighbouring pyridine ring. Protons 3 and 3' cannot be definitely assigned to a particular ring.

The spectrum of the complex $(Ru(4,4'\text{-diMebipy})_2acac)^+$ is very similar to that of the ammonia complex, except that there is some overlapping of the peaks associated with the 5 and 6' protons. The proton resonances are all at slightly higher fields than those in the ammonia complex. For the series of complexes $(Ru(4,4'\text{-diMebipy})_3)^{2+}$, $(Ru(4,4'\text{-diMebipy})_2(NH_3)_2)^{2+}$ and $(Ru(4,4'\text{-diMebipy})_2acac)^+$, there is a general shift of the proton resonances to higher field. If the arguments concerning metal to bipyridyl π-bonding applied to the tris complexes are used here, it would appear that the π-bonding increases across the series. This is the opposite to the order of the total π-bonding in the complexes deduced from the position of the t_{2g} orbital

from the spectroscopic data presented in Chapter III. However, in the N.M.R. studies probably only the metal to bipyridyl π-bonding is being investigated and it is likely that this bonding is greater in the bis-(4,4'-dimethyl-bipyridyl) complexes than in the tris complex where the number of ligands competing for the π-electrons is greater. However it must be remembered that the analysis of the N.M.R. spectra used here is not at all rigorous. The anisotropic effects of neighbouring atoms could be very different in the tris complexes from those in the ammonia and acetylacetonato complexes. It is unfortunate that measurements on a larger range of complexes were not possible. The study of a wide range of similar complexes with the aid of refined calculations could assist in distinguishing some of the important factors operating in the complexes, and thus assist in interpretation of the electronic spectra of these complexes.

TABLE 11

N.M.R. SPECTRA OF 4,4'-DIMETHLYBIPYRIDINE COMPLEXES. PEAK POSITIONS.[a]

Compound and Solvent	$3^{(b)}$	$5^{(b)}$	$6^{(b)}$	$3',^{(c)}$	$5',^{(c)}$	$6',^{(c)}$
$(Fe(4,4'\text{-diMebipy})_3)^{2+}$ MeOH	522.0	444.0	444.0			
$(Ru(4,4'\text{-diMebipy})_3)^{2+}$ MeOH	517.0	445.0, 439.0	464.0, 458.0			
$(Os(4,4'\text{-diMebipy})_3)^{2+(d)}$ MeOH	508.0	432.4, 426.4	451.65, 445.75			
$(Fe(4,4'\text{-diMebipy})(CN)_4)^{2-}$ H_2O				462.2	433.2, 427.4	546.7, 541.0
$(Ru(4,4'\text{-diMebipy})_2acac)^{+(d)}$ MeOH	498.95	454.1, 448.0	518.0, 512.0	507.35	421.2, 415.2	457.1, 451.1
$(Ru(4,4'\text{-diMebipy})_2(NH_3)_2)^{2+(d)}$ MeOH	500.8	463.1, 457.5	547.0 541.5	511.6	424.7, 418.7	453.4, 447.4

(a) Peak positions in c.p.s. from T.M.S.

(b) Protons (see Fig.1) in ring trans to another 4,4'-diMethylbipyridyl nitrogen.

(c) " " " " " other coordinated ligand.

(d) Obtained by use of C.A.T. (see page 133).

TABLE 12

N.M.R. SPECTRA OF 4,4'-DIMETHYLBIPYRIDYL COMPLEXES

CHEMICAL SHIFTS OF PROTONS[c]

Compound[e]	(a)	3[d]	5[d]	6[d]	3'[d]	5'[d]	6'[d]	J_{56}[b]	$J_{5'6'}$[b]
$(FeL_3)^{2+}$	ν	522	444	444					
	δ	8.70	7.40	7.40					
$(RuL_3)^{2+}$	ν	517	442.5	460.5				6.0	
	δ	8.62	7.37	7.67					
$(OsL_3)^{2+}$	ν	508	429.85	448.25				5.95	
	δ	8.47	7.16	7.47					
$(FeL(CN)_4)^{2-}$	ν				462.2	430.4	543.8	5.75	
	δ				7.70	7.17	9.06		
$(RuL_2(NH_3)_2)^{2+}$	ν	500.8	460.6	544.3	511.6	421.7	450.4	6.0	5.55
	δ	8.35	7.68	9.07	8.53	7.03	7.51		
$(RuL_2acac)^{+}$	ν	498.95	451.2	514.9	507.35	418.45	453.85	6.0	6.05
	δ	8.32	7.52	8.58	8.46	6.97	7.56		

(a) ν = chemical shift from T.M.S. in c.p.s. δ = chemical shift from T.M.S. in p.p.m.

(b) J = coupling constants in c.p.s. (c) For numbering scheme for protons see Fig.1.

(d) 3,5,6 = protons in ring trans to another 4,4'-diMethylbipyridyl nitrogen; 3',5',6' = protons in ring trans to other coordinated ligand. (e) L = 4,4'-diMethylbipyridyl.

APPENDIX. EXPERIMENTAL METHODS

Electronic Absorption Spectra

Electronic absorption spectra in the range from ~41,000cm^{-1} to ~7,000cm^{-1} were recorded on a Shimadzu Multipurpose Spectrophotometer. The solutions used were contained in a one centimeter cell. All the spectra were recorded at least twice (and in some cases also on a Beckmann DK-2A ratio-recording spectrophotometer) to check reproducibility ($\pm$ ~100cm^{-1}).

In some cases an attempt was made to analyse the spectra into the component Gaussian curves. The method used was one based on inspection, and checked by calculation.

Many of the trivalent complexes were susceptible to reduction in solution. This could often be overcome by using acid solutions, and recording the spectra quickly. An alternative method, found to be quite satisfactory, was to run the spectra using chlorine water as a solvent (both the reference and the sample cells containing chlorine water solutions). The spectra generally remained constant over several hours.

The spectra of several trivalent complexes which were not sufficiently stable to be isolated were obtained by taking a solution of known concentration of the corresponding

divalent complex. Very small quantities of solid ceric ammonium nitrate were added, and the spectra were recorded after each addition. In many cases the existence of isobiestic points indicated the presence of only two absorbing species in the appropriate region. However, this method is unsatisfactory at energies above ~27,000cm^{-1}, as most oxidising agents, including the ceric ions, begin to have significant absorptions in this region. It is therefore difficult to obtain accurate measurements of the spectra of the intraligand bands of the bipyridyl complexes. However, an attempt to obtain the intraligand spectra of the complex $(Ru(bipy)_3)^{3+}$ indicated that the spectrum was similar to that of the osmium complex, $(Os(bipy)_3)^{3+}$, and it was felt that the spectrum of $(Ru(bipy)_3)^{3+}$ reported by Mason et al[70] is probably the spectrum of a solution containing both the trivalent complex and some divalent tris-complex. In the present work in all cases a spectrum corresponding to that of the appropriate divalent complex could be obtained by standing the oxidised solution for several hours or by adding a suitable reducing agent. Similar techniques using hydroxylamine or stannous chloride as a reducing agent were used to obtain the spectra of the divalent halogeno-complexes $(Ru(bipy)Cl_4)^{2-}$ and $(Ru(bipy)Br_4)^{2-}$ from the complexes $K(Ru(bipy)Cl_4)$ and $K(Ru(bipy)Br_4)$.

Nuclear Magnetic Resonance Spectra

The nuclear magnetic resonance spectra were recorded with a Varian A-60 spectrometer. Saturated solutions of the appropriate complexes in methanol were used, with tetramethylsilane as an internal standard. However, in many cases the solutions were not sufficiently concentrated to give an adequate spectrum. In these cases a "time averaging computer" (C.A.T.) was used. A few drops of dichloromethane were added to the solution to act as a trigger point. Generally about 25 runs were sufficient to give a well resolved spectrum.

However, some complexes gave no identifiable spectra, even after up to 250 runs, although several solvents (e.g. chloroform, water, dimethylsulphoxide) were tried to obtain more concentrated solutions. These included $(Fe(4,4'\text{-diMebipy})_2(CN)_2)$, $(Ru(4,4'\text{-diMebipy})_2(CN)_2)$ $(Ru(4,4'\text{-diMebipy})_2(NO_2)_2)$ and $(Ru(4,4'\text{-diMebipy})_2Cl_2)$. Several attempts were also made to obtain the spectrum of $(Ru(4,4'\text{-diMebipy})(acac)_2)$ in benzene or chloroform. However, it was necessary to "CAT" the spectrum, and in the time required to complete this, appreciable oxidation of the complex had occurred.

Solvents

The solvents used were purified and dried by standard

methods[103], and were generally stored over molecular sieves. Those solvents used for spectroscopic studies were checked to see that they showed no absorptions in the appropriate regions.

Infra Red Spectra

Infra red spectra of the complexes were recorded on a Perkin-Elmer 337 infra red spectrophotometer. Mulls in nujol or halocarbon, or potassium bromide discs were used. Low frequency infra red spectra of a number of complexes were also obtained on a Grubb-Parsons DM-4 spectrophotometer, but owing to the complexity of the spectra in this region few definite assignments of bands could be made, and no relevant information was obtained.

Analyses

Micro-analyses for carbon, nitrogen, hydrogen and sulphur were determined by the Micro-Analytical Laboratory, University of Otago, Dunedin. We would like to thank Dr A.C. Campbell for his work on the analyses of the osmium complexes. Halide analyses were determined gravimetrically as silver halides.

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